

ELECTRICAL CONTACTS TO P-TYPE
ZINC TELLURIDE AND GALLIUM NITRIDE

By

JEFFREY TODD TREXLER

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The electrical and structural properties of sputter deposited metal contacts to p-ZnTe or p-GaN have been studied using current-voltage (I-V), Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS). Contacts of Au on p-ZnTe were heat treated over a range of 150-350°C for times up to 90 minutes. As-deposited the contacts had a breakdown voltage of ~0.5 V. Heating at $T \geq 200^\circ\text{C}$ for 15 minutes resulted in ohmic behavior (linear I-V curves) due to formation of near-surface acceptors from doping by Au without interfacial phase formation. The maximum current density was found to be 2.3 A/cm^2 at 5 volts following a 250°C heat treatment for 15 minutes. Diffusion of Au, which resulted in a highly resistive contact at 350°C , was extensive and resulted in compound formation.

For p-GaN, Au contacts were sputter deposited while Ni/Au, Ni/C/Au, Pd/Au and Cr/Au contacts were deposited by electron beam evaporation. The contacts were heat treated from 200-600°C for times up to 30 minutes. Contacts of Pd/Au and Cr/Au were also rapid thermally annealed (RTA) at 900°C for 15 seconds. Analytical data showed that Au did not react with GaN up to 400°C, therefore a rectifying contact was observed. A Ni layer between the Au and GaN led to dissociation of the GaN at 600°C. Increased electrical transport by the Ni/Au contacts was attributed to increased doping of the GaN near-surface region by interfacial carbon contamination, where it was calculated that $2 \times 10^{19} \text{ cm}^{-3}$ C atoms were incorporated during annealing. Pd/Au contacts were rectifying as-deposited. Increased conduction was attributed to the formation of a Au:Pd solid solution below 400°C and dissociation of the GaN following a 900°C, 15 second RTA. Cr/Au contacts resulted in ohmic behavior with $\rho_c \leq 4.3 \times 10^{-1} \text{ } \Omega \text{cm}^2$ after a 900°C, 15 second RTA. The RTA caused Cr to dissociate GaN, allowing Cr to increase the near-surface doping density. It was postulated that Cr diffused into the near-surface region using an interstitialcy mechanism and formed substitutional acceptors on the Ga sublattice. Temperature dependent I-V measurements showed that charge transport from Ni/Au, Pd/Au and Cr/Au contacts have components of both thermionic emission and field emission,

with Cr/Au having the largest contribution from field emission transport.

CHAPTER 1 INTRODUCTION

Presently there is a strong desire to fabricate optoelectronic devices which emit light in the blue region of the visible spectrum. Light emitting diodes (LED's) and laser diodes (LD's) emitting in this spectral region have found applications in optical data storage and full color displays. The present optical storage industry is dominated by AlGaAs/GaAs based devices which operate in the near infrared (IR) region. By replacing the infrared devices with shorter wavelength blue emitting devices, the beam can be focused to half the minimum spot size of the longer wavelength devices, yielding the ability to write four times as much data in the same surface area [And93]. The growing interest in bright full-color displays has also magnified the need for blue light emitting devices. Semiconductor optical devices routinely operate from the IR to green wavelengths. If this range could be extended into the blue wavelengths, semiconductor components could then emit and detect the three primary colors of the visible spectrum which would have a major impact on imaging and graphics applications [Str92]. This need for materials which emit in the blue region with high brightness and efficiency has

stimulated significant research, and while the materials and devices have been difficult to develop, great advances have been made in recent years.

There are two groups of blue light emitting materials that are viable for optoelectronic devices. These are the materials systems based on ZnSe or GaN. ZnSe is a direct band gap II-VI compound semiconductor with a zincblende structure, a 5.688 Å lattice parameter [Wea76], a band gap of 2.67 eV [Shi80] and an electron affinity of 4.09 eV [Swa66] at room temperature. ZnSe, doped n-type, has been grown using Cl doping during molecular beam epitaxial (MBE) growth [Ohk87], and p-type using a N₂ radio frequency (RF) discharge during MBE growth [Par90]. This ability to produce both n- and p-type doping has led to the fabrication of ZnSe based light emitting diodes (LEDs) [Qui93] and laser diodes (LDs) [Haa91] which emit in the blue to green wavelengths of 490-516 nm. Presently, the longest lifetime devices for laser output consist of a ZnCdSe/ZnSSe/ZnMgSSe single quantum well separate-confinement heterostructure laser diode with a wavelength of 514.7 nm, which operated more than 100 hours at room temperature under continuous wave (CW) operation [Tan96].

The other material used for blue light emitting devices, GaN, is a direct band gap III-V compound semiconductor commonly grown in the wurtzite crystal structure with lattice parameters of $a=3.189$ Å and $c=5.185$

Å [Maru69], a band gap of 3.4 eV [Str92] and an electron affinity measured to be between 3.3 eV [Nem96] and 4.1 eV [Pan74] at room temperature. GaN has been grown by metalorganic chemical vapor deposition (MOCVD) and doped n-type with Si donors [Nak92a], and p-type using Mg acceptors [Nak92b]. The ability to grow both n- and p-GaN led to the fabrication of p-GaN/n-InGaN/n-GaN double heterostructure blue LEDs with a peak wavelength of 440 nm and InGaN multi-quantum well (MQW) laser diodes capable of continuous wave operation at room temperature with a peak wavelength of 400.23 nm [Nak97].

Currently, GaN based LEDs are the only commercially available blue light emitting devices. This fact notwithstanding, there are still many areas which require further advancement before high quality, long life commercial devices can be manufactured and marketed. One of the critical problems facing these laser diodes is the short lifetime under either pulsed or CW operation. Poor contact performance, particularly in the p-type contact, is a contributing factor to poor device lifetimes.

An ohmic contact is a non-rectifying metal/semiconductor contact which exhibits linear current vs. voltage (I-V) characteristics and has a negligible resistance in comparison to the bulk resistance of the semiconductor. Ohmic contacts allow power to be efficiently

applied to the active region of the device as opposed to being consumed in the contacts.

This work will focus on improving the current contact schemes to p-ZnSe and p-GaN, and to give an understanding of the processes responsible for the formation of long-lived robust ohmic contacts to these materials. Background information on ohmic contacts and a discussion of the metallization schemes used and their effects of the interfacial reactions between metal and semiconductor will be presented.

A review of the literature is presented in chapter two. Metal/semiconductor contact theory and processes utilized in the formation of ohmic contacts are discussed. Then the literature on growth and doping is presented, focussing primarily on the formation of p-type material. This is followed by the various contact schemes that have been investigated for these materials. This information will first be presented for the II-VI materials ZnSe and ZnTe and then for the III-V material GaN.

Chapter three presents the experimental procedure followed in this study. The deposition and processing parameters are first presented. This is followed by a review of the characterization techniques used to study the electrical properties, surface composition, surface morphology, structural properties and interfacial reaction products.

The results and discussion of the contact studies are presented in chapters four and five. Chapter four presents the data on Au/p-ZnTe contacts. Heat treatments are described that lowered the breakdown voltage in these contacts and led to the formation of ohmic contacts. The composition and structure of the contacts were analyzed to identify changes induced by the heat treatments, which led to the ohmic behavior and the eventual breakdown of the ohmic contacts. In chapter five, the data for Au, Pd/Au, Ni/Au, Ni/C/Au and Cr/Au on p-GaN are presented with emphasis on the interfacial reactions upon heat treatment and conduction mechanisms in these contacts. Conclusions from these studies are summarized in chapter six and suggested future research is discussed in chapter seven.

CHAPTER 2 REVIEW OF THE LITERATURE

Schottky and Ohmic Contacts

When a metal and semiconductor are brought into electrical contact a potential barrier arises from the separation of charges at the metal-semiconductor interface such that a high resistance region devoid of mobile carriers is created in the semiconductor [Sha84]. Two types of contacts arise from this orientation: ohmic contacts, which are defined as a metal-semiconductor contact that has a negligible contact resistance relative to the bulk or spreading resistance of the semiconductor [Sze81], and Schottky contacts which rectify current flow across the metal-semiconductor interface. Most metal/semiconductor contacts are Schottky in nature.

Figure 2.1A shows metal and p-type semiconductor energy bands before contact. In this figure, Φ_m and Φ_s are the metal and semiconductor work functions, defined as the amount of energy required to raise an electron from the Fermi level to the vacuum level; χ_s is the semiconductor electron affinity, the energy difference between the vacuum level and the lower edge of the conduction band; and E_g is

the semiconductor bandgap. In Figure 2.1B the metal and p-type semiconductor have been brought into electrical contact in thermal equilibrium. When $\Phi_m < \Phi_s$, electrons flow from the metal into the semiconductor until the Fermi level on the two sides are aligned. After reaching the semiconductor, the electrons recombine with the majority carrier holes giving rise to a space charge layer of ionized acceptors. The concentration of holes in the space charge region is negligibly small compared to the acceptor concentration. It follows, that on the semiconductor side of the contact the space charge region consists of a depletion layer whose thickness W depends on the concentration of ionized acceptor atoms. In this configuration the obstacle to current conduction in contact/p-type semiconductor systems is the energy barrier at the valence band (Φ_b) which can be defined as:

$$\Phi_b = \chi_s + E_g - \Phi_m. \quad (2.1)$$

From this equation and Figure 2.1B, it can be seen that for non-degenerately doped semiconductors, where $\chi_s + E_g > \Phi_s$, a non-rectifying contact should be observed for a metal work function greater than the semiconductor work function.

This dependence of Φ_b on Φ_m is known as classical Schottky theory and is only observed in predominantly ionic semiconductors. For covalently bonded semiconductors Bardeen [Bar47] pointed out the importance of localized surface states in determining the barrier height. Dangling

bonds formed due to the covalent nature at the surface give rise to localized energy states at the semiconductor surface with energy levels lying in the forbidden gap. These surface states may be continuously distributed or localized in the band gap and modify the charge in the depletion region affecting the barrier height. These states are characterized by a neutral level Φ_0 . The effect of these surface states on the energy levels in a metal/p-type semiconductor can be seen in Figure 2.2. When equilibrium is reached, holes from the semiconductor adjacent to the surface occupy states below Φ_0 and the Fermi level at the surface aligns with that in the bulk. The surface then becomes positively charged and a depletion layer consisting of ionized acceptors is created in the semiconductor region near the surface. Because of this dipole formation, a potential barrier looking from the surface towards the semiconductor is obtained even in the absence of a metal contact. When a metal is now brought into contact with the semiconductor and equilibrium is reached, the Fermi level in the semiconductor must change by an amount equal to the contact potential by exchanging charge with the metal. If the density of surface states at the semiconductor surface is very large then the charge exchange takes place largely between the metal and the surface states, and the space charge in the semiconductor remains almost unaffected. As a result the barrier height becomes independent of the metal

work function and is given by:

$$\Phi_b = E_g - \Phi_0. \quad (2.2)$$

This barrier height is said to be "pinned" by the surface states. With Fermi level pinning playing a large role in the choice of contact materials, the ability to predict and determine whether this phenomenon will occur is of utmost importance.

In a model applicable to all semiconductors [Bar47], the Schottky barrier height, Φ_b , can be expressed as:

$$\Phi_b = S^*(s)\chi_m + \Phi_0(s), \quad (2.3)$$

where m and s refer to the metal and semiconductor, respectively, and $\Phi_0(s)$ represents the contribution of the surface states. The interface index $S^*(s)$ expressed as:

$$S^*(s) = d\Phi_0/d\chi_m, \quad (2.4)$$

gives the dependence of barrier height on the metal electronegativity, and χ_m is the metal electron affinity which is analogous to the metal work function. For covalently bonded materials, Φ_0 is large and nearly constant therefore S^* is nearly zero and Φ_b is nearly independent of χ_m . Ionic semiconductors, on the other hand, have a large S^* and Φ_b is expected to increase linearly with χ_m . Kurtin et al. [Kurt69] have suggested that S^* is a function of the electronegativity difference between cation and anion, (ΔX) , of compound semiconductors which is a measure of the ionicity of the material, and they have plotted these data as shown in Figure 2.3. The regime where $S=1$ is for ionic

bonding, while the tail near $S=0$ is for covalent bonding. This plot can be used for a rough estimate as to whether Fermi level pinning will occur; it is not an exact determination of bonding character. One example is the case of SiO_2 , which is strongly covalently bonded but has a $\Delta X = 1.7$.

There are also two other types of interfaces prevalent in metal/semiconductor contacts. These are reactive interfaces and samples with an insulating, non-reactive interfacial layer [Sha84]. The majority of work on reactive interfaces has dealt with silicides e.g. [Ott80, Fre80, Bri78], and will not be illustrated here. In most metal-semiconductor contacts before metal deposition, the semiconductor surface is prepared by chemical cleaning and a thin insulating oxide layer is invariably left on the surface of the semiconductor. When the interfacial layer is thin enough (i.e. $< 20\text{\AA}$), the potential drop across it is negligibly small compared to that in the semiconductor depletion region. Such a thin layer is transparent to the electrons as the electrons can tunnel through in either direction. Because of this, the barrier height Φ_b and the contact potential difference V_i may be unaffected by the presence of a thin interfacial layer [Sha84]. Thicker interfacial layers however, may increase Φ_b .

One final effect on the measured barrier height is a result of the electric field in the depletion region which

leads to image force barrier lowering. This effect occurs whether or not an interfacial oxide is present, and the magnitude of barrier lowering, $\Delta\phi_b$, is given by:

$$\Delta\phi_b = [(q^3 N_d / 8\pi^2 \epsilon_d^2 \epsilon_s) * (V_i - V)]^{1/4}, \quad (2.5)$$

where N_d is the carrier concentration, ϵ_d is the dielectric constant in the depletion region, ϵ_s is the dielectric constant in the bulk semiconductor ($\epsilon_d = \epsilon_s$) and V_i is the built-in potential of the barrier which is related to the position of the Fermi level. Since image force lowering of the barrier results from the field produced by an electron, the measured barrier height is not lowered by those methods which do not require movement of the electron over the barrier, (e.g. capacitance-voltage method).

Carrier Transport

Current flow in a metal-semiconductor junction occurs from charge transport between the metal and semiconductor. There are four mechanisms by which this can occur in Schottky contacts: a) thermionic emission over the barrier; b) tunneling through the barrier; c) carrier recombination (or generation) in the depletion region; and d) carrier recombination in the neutral region of the semiconductor which is equivalent to minority carrier injection (Figure 2.4 [Sha84]). In general semiconductor current transport described by classic Schottky theory is determined by the carrier concentration in the

semiconductor. At moderate temperatures (300K), mechanisms c and d dominate for very low carrier concentrations ($\sim 10^{14} \text{ cm}^{-3}$) and are rarely used to form low resistance ohmic contacts. For low carrier concentrations ($N_D \leq 10^{17} \text{ cm}^{-3}$), conduction across the metal-semiconductor interface is dominated by thermionic emission (TE) over the potential barrier, which is the case for Schottky barrier junctions. For higher carrier concentrations ($N_D \geq 10^{19} \text{ cm}^{-3}$), the barrier width becomes narrow and conduction may take place by tunneling through the thinned barrier, which is also known as field emission (FE) transport [Sze85]. Ohmic conduction is related to a large tunneling component. There also exists a hybrid case known as thermionic field emission (TFE), which is actually the mechanism (b) shown in Figure 2.4, in which there is enough kinetic energy for the carrier to be excited from the ground state to a level at which the potential barrier is thin enough for tunneling to occur. The conditions under which each conduction mechanism is expected to control current flow are fundamental to understanding formation of ohmic contacts.

Models to determine the dominant conduction mechanism have been devised for thermionic emission and field emission. These models allow evaluation of conduction mechanism from the current-voltage characteristics of the metal/semiconductor contact. A model for thermionic emission over a barrier was presented by Wagner [Wag31] and

Schottky and Spenke [Sch39]. In reverse bias the current is given by:

$$I = I_0 [\exp(-qV_R/kT) - 1], \quad (2.6)$$

where

$$I_0 = SA^*T^2 \exp[(\Delta\Phi_B - \Phi_B)/kT], \quad (2.7)$$

and A^* known as Richardson's constant is given by:

$$A^* = 4\pi m^* q k^2 / h^3. \quad (2.8)$$

In these equations I_0 is the saturation current, q is the electron charge, V_R is the reverse bias, k is Boltzmann's constant, S is the diode area, $\Delta\Phi_B - \Phi_B$ is the effective barrier height with $\Delta\Phi_B$ determined from Equation 2.5 for image force reduction, m^* is the majority charge carrier effective mass, and h is Planck's constant.

Tunneling can occur in a Schottky barrier junction in either forward or reverse bias. The probability of tunneling from the semiconductor to the metal increases as the doping density of the semiconductor increases or as the potential barrier decreases, e.g. through proper choice of the contact metal for an unpinned Fermi level. As mentioned before, when a metal and semiconductor are brought into electrical contact, a bending of the semiconductor bands occurs due to formation of a region depleted of free carriers whose thickness W (depletion width) is given by [Sze81]:

$$W = [(2\epsilon_s / qN_D) |V_i - V|]^{1/2}, \quad (2.9)$$

where N_D is the doping density, V_i is the built-in barrier

as discussed earlier, and V is the applied bias. This depletion width is shown in Equation 2.9 to be inversely proportional to the square root of the carrier density in the semiconductor. If the tunneling component dominates the current flow, the tunneling current can be given by the expression:

$$J_t \sim \exp(-q\Phi_B/E_{00}), \quad (2.10)$$

where E_{00} is a tunneling parameter proportional to $(N_D)^{1/4}$ which will be described in detail later in this section. Equation 2.10 thus indicates that the tunneling current will increase exponentially with $(N_D)^{1/4}$, and from Equation 2.9 the tunneling probability is proportional to $\exp(\Phi_B/W)$.

At higher temperature a significant number of carriers are able to rise to an energy where there is a thinner, lower barrier and tunneling can occur above the ground state (i.e. bottom of conduction band for electrons) but below the top of the barrier. Since the number of electrons decrease rapidly with energy above the Fermi level due to electron occupation probability, there exists an energy E_m (measured relative to the bottom of the conduction band) at which the contribution of TFE becomes maximum. For a semiconductor in which the Fermi level is not pinned, the magnitude of this potential barrier can be reduced for p-type materials by using a metal with a large work function, which will align the Fermi level as closely as possible to the semiconductor valence level.

Tunneling through a Schottky barrier has been analyzed theoretically by Padovani and Stratton [Pad66] and Crowell and Rideout [Cro69] with the following relationships being predicted:

$$I = I_s \exp(-qV_R/E_0), \quad (2.11)$$

where

$$E_0 = E_{00} \coth(E_{00}/kT), \quad (2.12)$$

and

$$E_{00} = (qh/4\pi) (N_d/m^*e_s)^{1/2}, \quad (2.13)$$

where the symbols have their usual meanings and the pre-exponential factor I_s is only weakly dependent on voltage and is a complicated function of barrier height, properties of the semiconductor, and the temperature. The energy E_{00} is an important parameter in tunneling and kT/E_{00} is a measure of the relative importance of TE versus FE [Pad71]. At low temperatures E_{00} may become large compared to kT , then $E_0 = E_{00}$ and field emission dominates. At high temperatures where $E_{00} \ll kT$, then $E_0 = kT$ and thermionic emission dominates. For intermediate values of temperature, $E_{00} \approx kT$ and thermionic field emission transport dominates current transport.

Interfacial Reactions

Interfacial reactions may also play a large role in the formation of ohmic contacts. A review by Kim et al. [KimTJ97] demonstrated the role of interfacial reactions for

ohmic contacts to wide bandgap semiconductors. Heat treatments are often used to form tunneling contacts by alloying between the contact metal and the semiconductor [Hal50]. The simplistic idea is to choose a metal or metals (elements) which create a highly doped semiconductor region and leads to ohmic behavior through tunneling transports. In other cases, heat treatments result in interfacial compounds, such as metal/silicide/silicon contacts. In these contacts, the metal/semiconductor interface is eliminated and replaced by two new interfaces, a metal/compound and a compound/semiconductor interface.

The most widespread use of interfacial reactions to form ohmic contacts has been in GaAs. The consequences of these interfacial reactions vary, but dissociation of the compound semiconductor is a necessary, but not sufficient condition for formation of good contacts. In those cases where decomposition results in an ohmic contact, the surface doping concentration is generally increased [Hol97]. The proposed mechanism for this incorporation of dopant is an epitaxial regrowth of the GaAs with the regrown layer having an increased dopant concentration. Sands et al. [San88] documented epitaxial regrowth of GaAs at the reaction interface for the specific case of Si/Ni/GaAs. Through a series of heat treatments, (250°C for 30 minutes followed by 350°C for 30 minutes) they detected a regrown GaAs region using XTEM. Holloway et al. [Hol91] showed that interface

segregation of Si dopants may also occur in the region of decomposed GaAs. This was the first direct proof that segregation of dopant from the semiconductor (as opposed to lattice incorporation from the metallization) could lead to ohmic contact formation.

II-VI Materials

Growth and Doping

ZnSe epitaxial layer growth

II-VI compound semiconductors such as ZnSe ($E_g=2.67$ eV at RT) have long been promising materials for the fabrication of efficient blue light emitting diodes [Qiu91]. One of the objectives of this work is to understand the factors in the formation of ohmic contacts to p-doped II-VI wide bandgap semiconductors, so growth and doping of these p-type materials will be discussed in this section.

Initial efforts to incorporate a substitutional acceptor impurity into ZnSe during crystal growth focused on lithium doping during molecular beam epitaxial (MBE) growth [Dep89]. Lithium was shown to have a maximum net acceptor density of $1 \times 10^{17} \text{ cm}^{-3}$, above which strong compensation occurred resulting in highly resistive ZnSe. In addition, Li is mobile in ZnSe and doping was non-reproducible. Oxygen has also been reported as a non-reproducible dopant

in ZnSe layers grown by MBE, [Aki89] with the largest reported net acceptor density of $1.2 \times 10^{16} \text{ cm}^{-3}$. In 1990, Park et al. [Par90] introduced a novel doping technique using nitrogen atom beam doping from an RF discharge source during MBE growth. Repeatable net acceptor concentrations as large as $3 \times 10^{17} \text{ cm}^{-3}$ were reported using this technique. More recently a maximum value of $N_A - N_D = 1.8 \times 10^{18} \text{ cm}^{-3}$ was reported by Ohtsuka et al. using an electron cyclotron resonance (ECR) plasma source [Oht93].

ZnTe epitaxial layer growth

The wide-bandgap semiconductor ZnTe ($E_g = 2.3 \text{ eV}$) is a II-VI material which has been used to form ohmic contacts to p-ZnSe [Hie93]. Although bulk crystal ZnTe is naturally doped p-type by an intrinsic defect, considerable difficulty has been experienced in achieving reproducible, high quality p-type ZnTe using MBE. Such difficulty has generally been associated with the physical incorporation of the dopant species due to a low sticking coefficient [Han93]. For example, Kitagawa et al. [Kit81] investigated antimony doping at flux levels greater than those of the host elements, with the $F_{\text{Te}} = 2F_{\text{Zn}}$. Doping levels of $1 \times 10^{18} \text{ cm}^{-3}$ were reported for ZnTe homoepitaxially grown on ZnTe substrates. Hishida et al. [His89] used elemental phosphorus to obtain p-doping of ZnTe grown by MBE on GaAs substrates. They found that the best films were grown with a Te/Zn beam pressure ratio (BPR) of 4. A maximum doping of $4 \times 10^{17} \text{ cm}^{-3}$

was obtained with phosphorus beam equivalent pressure comparable to that of Te. However, the crystalline quality deteriorated with this doping, as shown by a broad x-ray rocking curve. Han et al. [Han93] succeeded in obtaining doping levels exceeding 10^{19} cm^{-3} in ZnTe by employing the same types of nitrogen sources used to dope ZnSe. The crystalline quality of ZnTe was maintained.

Schottky and Ohmic Contacts

ZnSe

Many successful ohmic contact schemes to n-ZnSe have been reported and have been reviewed by Fijol and Holloway. [Fij96a] An important factor for ohmic contacts is Fermi level pinning, and experimental data has been collected indicating that Fermi level pinning does not occur with ZnSe [Che94, Xu88, Hol97]. Thus ohmic contacts should be predicted by the metal work function as long as interfacial contamination and oxide layers do not interfere with charge transport between the metal and ZnSe. However, with the electron affinity of ZnSe equal to 4.09 eV, and an $E_g = 2.67$ eV, ($E_g + \chi = 6.76$ eV), finding a metal with a large enough work function is impossible. Still, many metallization schemes have been studied for ohmic contacts to p-ZnSe. The most basic schemes consisted of non-graded single metal contacts. Fijol et al. [Fij95] investigated the effects of heat treatments on Au and Ag contacts to p-ZnSe and concluded

that both metals formed rectifying contacts with minimum breakdown voltages of 3.0 and 2.3 eV, respectively. The lower breakdown voltage for Ag was attributed to oxygen doping of the near-surface region. Pseudo-ohmic behavior for Au contacts was reported by Akimoto et al. [Aki91] by using an oxygen plasma to grow an interfacial oxide before metal deposition. They proposed that O doping occurred leading to the pseudo-ohmic behavior. Chen et al. [Che94] reported a decrease in the breakdown voltage of about 0.25 eV upon deposition of 2-3 monolayers of Se at the interface between the p-ZnSe and Au. All of these contacts were rectifying in nature.

A second contact scheme involved the semimetal HgSe. Lansari et al. [Lan92] used an *in-situ* MBE epitaxial layer of HgSe to reduce the semiconductor interfacial energy barrier to about 0.6 eV, and Fijol et al. [Fij96b] used an *ex-situ* process of reacting Hg with an *in-situ* Se capping layer to form HgSe. The potential barrier of this contact to p-ZnSe was measured to be ~0.55 eV, and it remained rectifying.

But the most successful efforts at ohmic contacts to p-ZnSe have incorporated ZnTe into the contact scheme. Fan et al. [Fan93] used a pseudograded Zn(Te,Se) structure sandwiched between a p-ZnTe top layer and a p-ZnSe bottom layer. The pseudograded contact region consists of 17 cells, each of 20Å thickness. In each cell both the

thickness of the ZnTe and ZnSe layers were varied. The first cell next to the p-ZnSe layer contained 18Å p-ZnSe and 2Å of p-ZnTe, the next cell 17Å p-ZnSe and 3Å p-ZnTe, and so on. It was proposed that this pseudograded band gap region allowed injection of holes from the heavily doped ZnTe into ZnSe. A specific contact resistance (ρ_c) of $2 \times 10^{-3} \text{ } \Omega \text{cm}^2$ was measured for these contacts with $N_A = 9.5 \times 10^{17} \text{ cm}^{-3}$. Hiei et al. [Hie93] employed p'-ZnTe/ZnSe quantum wells whose sub-bands were aligned in energy to allow resonant tunneling of holes through the multi-quantum well region. The ZnSe barriers were 20Å thick and the ZnTe wells varied from 3 to 17Å in thickness. This scheme also included a p-ZnTe capping layer. They recorded a ρ_c as low as $5 \times 10^{-2} \text{ } \Omega \text{cm}^2$ for ZnSe with a hole concentration of $7 \times 10^{16} \text{ cm}^{-3}$. Fijol and Holloway studied the thermal stability of this contact scheme and found them to be thermally unstable. They deteriorated badly under modest heating, or with high current densities ($\geq 1000 \text{ A/cm}^2$) [Fij96].

ZnTe

When graded or MQW contacts of ZnTe/ZnSe are used for ohmic contacts to p-ZnSe, an ohmic contact is required to p-ZnTe. For this contact both single and multi-layer metal contacts have been studied. Ozawa et al. [Oza93] investigated Au, Au/Pt, Au/Pd, and Au/Pt/Pd contacts to p-ZnTe and reported the lowest specific contact resistance of $\rho_c = 4.8 \times 10^{-6} \text{ } \Omega \text{cm}^2$ for Au/Pd annealed at 200°C. They proposed

that a reaction took place between Pd and ZnTe and assumed that this reaction was more likely to take place at elevated temperatures. The exact role of the Pd layer in the formation of the ohmic contacts was not determined. The contacts were not thermally stable, with an increase in specific contact resistance occurring after a 250°C, 3 minute anneal for all contacts, (e.g. an increase to $\rho_c = 2 \times 10^{-4} \text{ } \Omega \text{cm}^2$ for Au/Pd, after 200°C, 3 minutes). Mochizuki et al. [Moc94] investigated Au/Pt/Ti/Ni and proposed that the reaction between Ni and ZnTe lowered the specific contact resistance ($\rho_c = 7 \times 10^{-6} \text{ } \Omega \text{cm}^2$ as-deposited). Insertion of the Ti layer was reported to improve the thermal stability up to 350°C. In later work, this group detected formation of NiTe₂ from the reaction between Ni and ZnTe upon annealing at 300°C for 3 minutes, which apparently played an important role in the lowering of the specific contact resistance of Au/Pt/Ni/Ti [Moc95]. Finally, Ohtsuka [Oht95] investigated Au/p-ZnTe contacts using an oxygen plasma cleaning and HCl treatment before Au deposition. A Te-rich layer was formed on the surface. Specific contact resistances as low as $5.8 \times 10^{-6} \text{ } \Omega \text{cm}^2$ were reported on p-ZnTe ($N_A = 2 \times 10^{18} \text{ cm}^{-3}$). There was no mention of any reaction of Au with the underlying ZnTe.

III-V Materials

GaN Epitaxial Layer Growth and Doping

As previously mentioned, a second objective of this research was to understand the formation of ohmic contacts to p-GaN. The III-V nitrides, in particular GaN, are also promising materials for semiconductor device applications in the blue and ultra-violet (UV) wavelength regions [Str93]. InN, GaN, and AlN with direct band gaps of 1.9 eV, 3.4 eV, and 6.2 eV, respectively [Str93], can be grown in the wurtzite crystal structure to form a continuous alloy system with the ability to grade the wavelength of the emitted light over the entire visible spectrum.

However, two intrinsic material problems have inhibited the growth of high quality p-GaN. First, no lattice matched substrate for GaN has been found so all films have had a large defect density ($\sim 10^{10-12} \text{ cm}^{-2}$). Second, GaN intrinsically dopes n-type. The methods and treatments discovered to overcome these difficulties and resulting production of high quality p-GaN will be discussed below.

Substrates

Despite the large lattice mismatch (-14%) and the difference in thermal expansion coefficients, the majority of GaN growth studies have used the basal plane (0001) of sapphire (Al_2O_3) [Str92]. Other substrates investigated with limited success have included SiC [Kim94 and Bot95],

ZnO [Sit90], and MgO [Pow90], all of which are zinc-blende crystal structure. More recently Kuramata et al. [Kura95] and George et al. [Geo96] have grown GaN on the (111) and (100) planes of magnesium aluminate (MgAl_2O_4) which has a spinel crystal structure and a lattice mismatch of $\sim 10\%$ with GaN. One of the advantages of this substrate and SiC is the ability to cleave (not possible with sapphire) which provides the possibility of facets to be used as a cavity mirror in a laser diode.

Lithium aluminate (LiAlO_2) and lithium gallate (LiGaO_2) single crystals are also attracting attention as substrates for epitaxial growth of GaN [Nic96]. The small mismatches with GaN (-1.5% for LiAlO_2 and 0.2% for LiGaO_2) should lead to lower defect concentrations [Wil96]. However, the crystal quality of MBE grown GaN films on LiGaO_2 , as determined by photoluminescence (PL) measurements, was similar to films grown on sapphire. This was attributed to the presence of strain due to the difference in thermal expansions coefficients between layer and substrate [And97]. More recent work has occurred on GaN layers grown homoepitaxially on bulk single crystal GaN using MBE [Gas96] and metalorganic chemical vapor deposition (MOCVD) [Pon96]. While homoepitaxial approaches are promising, the quality of epilayer GaN has not improved dramatically ($\rho_i \sim 10^7\text{--}10^8 \text{ cm}^{-2}$).

Buffer layers

Sapphire is still the primary substrate for GaN growth, therefore all research groups have used low temperature buffer layers between the substrate and GaN film. The purpose of these buffer layers is to reduce the detrimental effects of the lattice mismatch by trapping defects in the layer and not allowing them to propagate to the deposited film. Amano et al. [Ama90] used a 500Å thick AlN buffer layer grown at 600°C and Khan et al. [Kha92] used a 250Å thick AlN layer grown at 550°C. Nakamura et al. [Nak94] have incorporated a 250Å GaN buffer layer grown at 500°C. In all these cases, the buffer layers were grown by MOCVD. More recently, Li et al. [Li95] have reported that a double buffer layer with GaN and AlN as the first and second layers leads to mirror-like films across the entire substrate. Kuznia et al. [Kuz93] investigated the crystalline quality of both GaN and AlN buffer layers grown at 500°C. They determined, using low-energy electron diffraction (LEED) and cross-sectional transmission electron microscopy (XTEM), that the AlN buffer layer was amorphous upon deposition and become single crystal following deposition of the GaN epitaxial film at 1000°C. Under similar conditions, the GaN buffer layer was also amorphous before GaN epilayer growth, and then appeared to convert mostly to single crystal form with some buried polycrystalline or amorphous regions.

Autodoping

As pointed out earlier, unintentionally doped GaN has in all cases been observed to be n-type [Str92]. There is no consensus on the cause of this autodoping, but many believe nitrogen vacancies are the intrinsic defect responsible for n-type conductivity [Pan73a]. By proper growth, the electron concentrations of GaN doped with Si were in the range of 10^{17} - 2×10^{19} cm⁻³ [Nak92a].

Many potential p-dopants have been investigated, including Zn and Mg [Maru69] and Be and Li [Pan73b], with all showing highly compensated material in the absence of post-deposition treatments. In addition to compensation of donors resulting in semi-insulating layers, low activation of the acceptor species was also observed. One of the causes of this low activation is the relatively deep level of acceptors in GaN. For example, the ionization level of Mg in GaN is ~150-165 meV [Aka91]. This limits the electrically active acceptors at room temperature to less than 1% of substitutional Mg. This leads to the discrepancy between dopant concentration and free hole concentration. Currently using Mg, in order to obtain 1×10^{17} cm⁻³ free holes, there would need to be 1×10^{19} cm⁻³ Mg atoms in the GaN. At this time, there is no shallow acceptor known for GaN to overcome this problem.

Along with the relatively deep acceptor levels in p-GaN, low activation was also attributed to introduction of

hydrogen during the growth of GaN, leading to an in-situ hydrogenation process which caused the formation of acceptor-H neutral complexes and compensation [Nak92b]. This conclusion was supported by Brandt et al. [Bran94] who investigated intentional hydrogenation of acceptors and found a reduction in hole concentration due to the formation of H-acceptor complexes. Pearton et al. [Pea96a] studied the role of atomic hydrogen introduced during processing in passivating the electrical activity of Mg and C acceptors using secondary ion mass spectrometry (SIMS). They determined that H had a diffusivity of $>10^{-11} \text{ cm}^2\text{s}^{-1}$ at 170°C and passivated the Mg and C acceptors. They found that annealing at $450\text{--}500^\circ\text{C}$ restored the electrical activity, but the hydrogen did not physically leave the films until much higher ($\sim 800^\circ\text{C}$) temperatures. In another study with H ion implanted samples, they determined that the dissociation of Mg-H complexes and the loss of hydrogen from GaN were sequential processes. Reactivation occurred at $\leq 700^\circ\text{C}$ annealing under N_2 , while significant concentrations of hydrogen remained in the crystal even at 900°C [Pea96b]. In another approach to re-activate the dopant, Amano et al. used a low-energy electron beam irradiation (LEEBI) process with the accelerating voltage far below the threshold energy for atom displacement. They achieved a hole concentration of $2 \times 10^{16} \text{ cm}^{-3}$ [Ama89]. The LEEBI treatment was limited to the penetration depth of the electron beam, therefore only a

thin surface layer was converted to p-type material. On the other hand, N_2 annealing re-activated the dopant throughout the entire epilayer.

Attempts to limit the presence of H in the growth environment have also been reported. Abernathy et al. obtained a hole concentration of $3 \times 10^{17} \text{ cm}^{-3}$, doping with C introduced as CCl_4 using a He carrier gas [Abe95]. Zolper et al. obtained p-GaN using ion-implantation of Ca acceptors requiring an RTA treatment at 1100°C [Zol96a], while Brandt et al. have reported hole concentrations of up to 10^{19} cm^{-3} , with doping efficiencies of up to 10% at room temperature, grown by MBE with no post-deposition treatment [Bran94].

Contacts

With n-type material being much easier to grow than p-GaN, the large majority of ohmic contact studies are focused on n-GaN. In this section, advances made in contacting n-GaN are discussed and related to contact schemes for p-GaN. The contacts and heat treatments used to obtain low contact resistances are described as well as work investigating the interfacial reactions which lead to ohmic contacts. Finally, previously reported contact schemes for p-GaN will be reviewed.

n-GaN

A major topic of discussion for GaN is whether the Fermi level is pinned as for GaAs or is unpinned as for

ZnSe. A pinned E_F would lead to barrier heights not dependent on the metal work function. If E_F is not pinned, small work function metals should give lower potential barriers and form ohmic contacts to n-type materials, since the Schottky contact theory predicts that the barrier height is equal to:

$$\Phi_B = \Phi_M - \chi_S. \quad (2.13)$$

Recent studies have reported that the barrier height was not solely dependent on the metal work function. Guo et al. used capacitance-voltage (C-V) measurements to determine that Schottky barrier heights of Pt and Pd on n-GaN were 1.04 and 0.94 eV [Guo95]. They proposed that since the difference in work function between Pt and Pd was greater than the difference in measured Schottky barrier height, that Φ_m did not uniquely determine Φ_B . Wang et al. measured Pt and Pd Schottky diodes on GaN and reported no dependence of the barrier height on the difference between the metal work functions [Wan96].

Other work has also shown that the Fermi level is not pinned. Foresi and Moustakas deposited Al and Au contacts, and found Al to be ohmic as deposited while Au required a 575°C anneal to obtain ohmic characteristics. They speculated that Au ohmic contacts were due to Au diffusion into the GaN, but showed no evidence to support this speculation. This work supported the idea that the Fermi level was not pinned since $\Phi_{Al} < \Phi_{Au}$ (4.08 eV to 5.1 eV) and

$\Phi_{Al} < \chi_{GaN}$ (4.1 eV) [For93]. Miller and Holloway investigated Ag, Au, and Ti contacts and showed that as deposited Ag ($\Phi_{Ag}=4.3$ eV) contacts were weakly rectifying while Au provided strongly rectifying contacts. Ti ($\Phi_{Ti}=4.4$ eV) was rectifying as-deposited but became ohmic upon annealing due to the formation of a TiN layer [Mil96]. Finally, Fan et al. employed a Ti/Al/Ni/Au contact scheme with an in-situ reactive ion etching (RIE) before deposition to remove the surface oxide. They obtained a low specific contact resistance ($\rho_c=8.9 \times 10^{-8} \text{ } \Omega \text{cm}^2$) and speculated that the surface defect density following the RIE was not large enough to pin the Fermi level [Fan96].

Thus the data show that either the Fermi level is completely or only partially pinned. It is generally speculated that partial Fermi level pinning is due to interfacial contamination at the GaN surface rather than an intrinsic property of the semiconductor itself.

The majority of these studies concentrated on determining the mechanism of ohmic contact formation. Lin et al. grew an InN/GaN short period superlattice (SPS) sandwiched between a GaN channel and an InN capping layer. This SPS allowed greater tunneling to occur through sub-band states which led to specific contact resistances as low as $6 \times 10^{-5} \text{ } \Omega \text{cm}^2$, with GaN doped $\sim 5 \times 10^{18} \text{ cm}^{-3}$ without any post-annealing [Lin94a]. Another mechanism for ohmic contact formation has been to increase the probability of tunneling

by increasing the doping concentration of the near surface region, as discussed above. Since N vacancies act as donors in GaN [Jen89], increasing their concentrations either by high temperature anneals or interfacial reactions have been used. Lester et al. deposited non-alloyed Ti/Al contacts on Si implanted GaN where the ohmic character ($\rho_c = 1 \times 10^{-5} \Omega \text{cm}^2$) was believed to be due to the 1120°C implant activation anneal which generated nitrogen vacancies [Les96], Zolper et al. have collected Auger electron spectroscopy (AES) data to support the hypothesis that an AlN encapsulant will reduce N loss from the GaN substrate during an anneal at 1100°C. Without a capping layer, N loss may create an n' region at the surface [Zol96b]. Cole et al. investigated W contacts on n-GaN and concluded that upon annealing at up to 1000°C, formation of $\beta\text{-W}_2\text{N}$ and W-N interfacial phases were responsible for the ohmic behavior ($\rho_c = 8 \times 10^{-5} \Omega \text{cm}^2$ for $N_D = 1.5 \times 10^{19} \text{ cm}^{-3}$). They proposed that the N to form these phases out-diffused from the GaN without changing the original structure, leading to an accumulation of N vacancies near the GaN surface [Col96]. A similar result was reported for Ti/Al contacts, in which formation of a TiN_x interfacial phase was postulated to create N vacancies [Bin94]. Lin et al. have speculated that only 1-2 monolayers of TiN are needed to form N vacancies which would generate a 100Å layer of GaN with an electron density of 10^{20} cm^{-3} [Lin94b]. Ruvimov et al. detected a TiN layer by

XTEM at the Ti/GaN interface after annealing at 900°C [Ruv96]. Finally, Smith et al. investigated Al contacts and found the formation of a thin AlN layer on the surface led to increased carrier conduction, presumably due to increased N vacancies [Smi96].

Various other studies of multilayer contact schemes leading to either extrinsic doping of the near surface region or phase formation led to decreased contact resistances. Miller and Holloway postulated that in Au/Si/Ti contacts, Si diffused to the GaN surface and served as an n-type dopant [Mil96]. For PtIn, annealed at 800°C for 1 minute in a high purity Ar atmosphere, In was incorporated into the GaN lattice producing $(\text{In}_x\text{Ga}_{1-x})\text{N}$ and $\text{Pt}(\text{In},\text{Ga})_2$. Formation of $(\text{In}_x\text{Ga}_{1-x})\text{N}$ resulted in ohmic behavior with $\rho_c < 1 \times 10^{-3} \text{ } \Omega\text{cm}^2$ [Ing97]. Ping et al. showed that annealed Pd/Al/n-GaN contacts formed a Pd_2Al_3 phase with $\rho_c = 1.2 \times 10^{-5} \text{ } \Omega\text{cm}^2$ upon annealing at 650°C for 30 seconds [Pin96]. Luther et al. reported that Ti in Ti/Al contacts reduced the native interfacial oxides, Al diffused through the Ti to the interface, and an Al-Ti intermetallic formed which contacted the GaN. These contacts became ohmic upon annealing at 400°C for 3 minutes in an Ar/4%H₂ atmosphere ($\rho_c = 7 \times 10^{-6} \text{ } \Omega\text{cm}^2$ for $N_D = 5 \times 10^{17} \text{ cm}^{-3}$) [Lut97].

p-GaN

In contrast to n-GaN contacts, which have been widely studied, there is very little information on p-GaN contacts.

A limited number of studies have reported Schottky barrier heights and that interfacial contamination has limited contact formation. However, most reports simply mention the p-contact used in a particular device. There has been very limited information on the formation of interfacial phases or conduction mechanisms in p-GaN. Due to the large E_g (3.4 eV) and χ_s (4.1 eV) of GaN, a metal would need $\Phi_m \geq 7.5$ eV to achieve an ohmic contact with the Fermi level unpinned. Unfortunately there are no metals with work functions larger than 5.6 eV, [Sze81c] thus interfacial reactions, doping of the near surface region, or graded band offsets must be used for ohmic contact formation.

Two groups have reported the effect of metal work function on contact properties to p-GaN. Mori et al. measured the Schottky barrier heights and a contact resistances of Pt, Ni, Au and Ti to p-GaN. Their data showed both Φ_b and ρ_c decreased with increased metal work function, as expected for an unpinned Fermi level [Mor96]. Ishikawa et al. investigated the effects of surface cleaning on the electrical properties of metal/GaN interfaces, and measured ρ_c for Pt, Ni, Pd, Au, Cr, Ti, Al and Ta on p-GaN. They showed that removal of the interfacial contamination layer between the metal and the GaN did not significantly reduce the contact resistance. However, the resistance decreased exponentially with increased metal work function. Also no reaction between any of these metals and GaN could

be detected after annealing at temperatures below 500°C. It was proposed that for ohmic contacts, a metal is needed which would react with GaN during annealing at high temperatures [Ish97]. The remainder of information on p-GaN contacts consists of the metals used for devices. Early work on p-n junctions and p-GaN/n-InGaN/n-GaN double heterostructure blue Light emitting diodes (LEDs) used Au as the p-contact [Nak91 and Nak93]. Subsequently, a Ni interfacial layer was added between the Au and p-GaN [Nak95]. Other groups also used this Ni/Au scheme [Kha95] with Molnar et al. reporting thicknesses of 200Å Ni/2000Å Au [Mol95]. All subsequent reports by Nakamura et al. regarding their LEDs and laser diodes (LDs) used this Ni/Au scheme (e.g. [Nak96]). Other groups have used Ni [Sak95], Au + Zn [Kug95] and Ti/Mo/Au (non-ohmic) [Gol93]. None of these studies reported the electrical properties of the contacts or metallurgical reactions occurring between the metals and semiconductor. In summary, while there has been a great deal of work on n-GaN contacts, the understanding of contacts to p-GaN is very limited and needs to be elevated for GaN based blue light emitting devices to reach their potential.

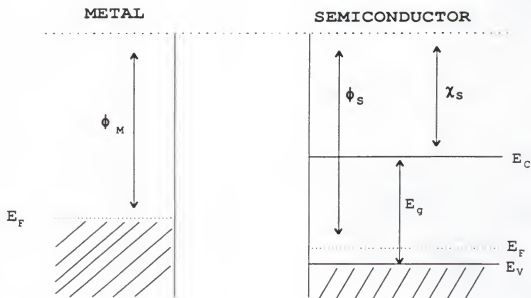


Figure 2.1A. Metal and p-type semiconductor before contact.

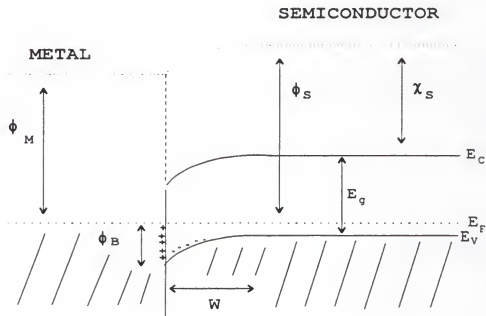


Figure 2.1B. Metal and p-type semiconductor in thermal equilibrium after the contact has been made.

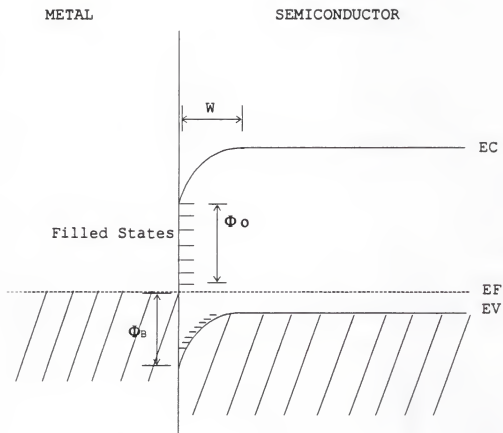


Figure 2.2. Metal/p-type semiconductor energy bands, showing the effects of surface states, after contact has been made.

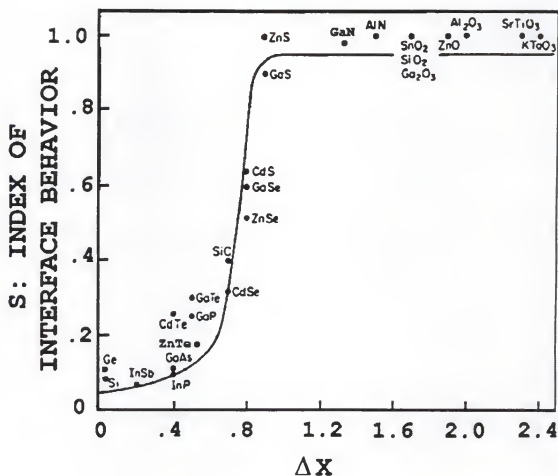


Figure 2.3. Index of interface behavior, S as a function of lattice electronegativity difference ΔX between the cation and anion for various semiconductors [Kur69].

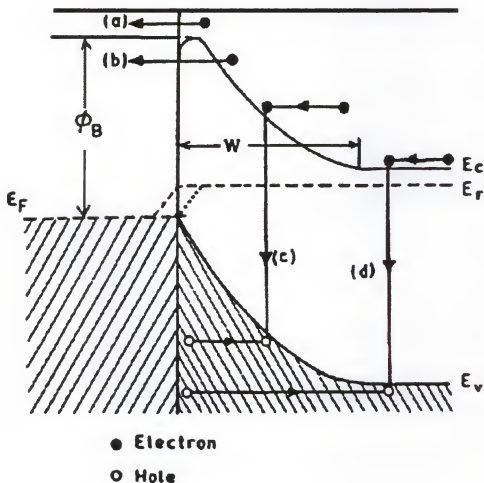


Figure 2.4. Energy band diagram of a forward biased Schottky barrier junction on an n-type semiconductor showing different transport processes; (a) thermionic emission, (b) thermionic tunneling through the barrier, (c) carrier recombination in the depletion region, and (d) hole injection from the metal into the semiconductor [Sha84d].

CHAPTER 3 EXPERIMENTAL PROCEDURE

Introduction

The following chapter describes the experimental process that was followed to prepare electrical contact samples to p-ZnTe and p-GaN. The procedure consisted of initial cleaning of the samples followed by metal contact deposition. These contacts were then heat treated and characterized in terms of their electrical properties, surface composition, surface morphology and interfacial reaction products.

Deposition and Processing

p-ZnTe Contacts

Investigation of Au contacts was performed on ZnTe/ZnSe samples grown on semi-insulating GaAs substrates using a custom made Molecular Beam Epitaxy (MBE) system and the sample configuration shown in Figure 3.1 [Jeo95]. An undoped 0.5 μm ZnSe buffer layer was epitaxially deposited on the GaAs, followed by a 2.3 μm p-ZnSe epilayer. The ZnSe/ZnTe multi-quantum well (MQW) structure described by

Hiei et al. [Hie93] was epitaxially deposited onto the p-ZnSe layer. The MQW structure was capped by a 1100Å heteroepitaxial p-ZnTe layer. An Oxford Applied Research Systems nitrogen free radical source was used for the p-type dopant layers. The free hole density was measured by a Hall experiment to be $\sim 3 \times 10^{18} \text{ cm}^{-3}$.

No further surface preparation was done on the as-grown ZnTe samples before metal deposition. The Au contacts were deposited by sputtering [Ohr92] in a custom built sputter deposition system [Tru92]. The system contained two radio frequency (RF) and two direct current (DC) 2" diameter planar magnetron sputter guns manufactured by US Inc. The vacuum chamber was a quartz bell jar with a Viton seal, seated on a stainless steel base plate. The system consisted of a liquid nitrogen cooled (trapped) diffusion pump (Varian VH5-6) which was backed by a Sargent-Welch mechanical pump, model #1397. The ultimate pressure reached by the system was $\sim 2 \times 10^{-7}$ Torr.

For deposition, the samples were loaded in the sputter chamber (Figure 3.2) which was pumped to a base pressure of at least 2×10^{-6} Torr. The 1500Å thick Au contacts were deposited from a 2 inch Pure Tech Inc. sputter target, (99.99% purity) using a DC sputter gun with a potential of 375 V, and a power of ~ 100 W. The gas pressure was 18 mTorr argon and a deposition rate of $\sim 188 \text{ Å/minute}$ was achieved. To improve the uniformity of the film thickness, the sample

was rotated about the system axis at 25 rpm. The Au contacts were patterned as dot contacts (0.8 mm diameter) during deposition using a stainless steel shadow mask. This method resulted in electrically isolated discrete Au dot contacts separated by ~ 0.4 mm (Figure 3.3).

Following deposition, the samples were heat treated in a quartz tube furnace in flowing forming gas (10% H_2 , 90% N_2). Separate Au/ZnTe samples were individually heat treated at 150, 200, 250, or 350°C using 15 minute increments for total times up to 90 minutes.

p-GaN Contacts

Metal contacts were deposited on a variety of GaN epitaxial films grown by metalorganic chemical vapor deposition (MOCVD) on a polycrystalline GaN buffer layer on a (0001) sapphire substrate [Kha91]. Mg acceptors were used to obtain p-type conduction and carrier concentrations at 296K were measured by a Hall technique to be between 5×10^{16} – 4.5×10^{18} cm^{-3} . The contact schemes investigated consisted of Au, Ni/Au, Ni/C/Au, Pd/Au, and Cr/Au with the first metal listed being deposited first and adjacent to the GaN. All samples were degreased prior to deposition using acetone, methanol, and de-ionized water (DI H_2O) for 5 minutes followed by a N_2 blow dry. Any native oxide was removed using a 10:1 DI:HCl etch for 5 minutes followed by a 5 minute DI rinse and N_2 blow dry. The samples were then

immediately introduced to the deposition chamber.

The 2000Å thick Au contacts were DC magnetron sputter deposited using the previously described sputter system and the same target as was used for the Au/p-ZnTe contacts. For GaN contacts, the sputter atmosphere was 25 mTorr Ar with a power of 40 W. For all GaN contacts, a smaller stainless steel shadow mask was used which defined contacts with a diameter of ~0.5 mm and a spacing of ~0.2 mm.

All contacts other than Au were deposited in a Davis Wilder vacuum system with an Airco Temescal four pocket electron beam evaporator [Ohr92], powered by a model ES-6 power supply (Figure 3.4). The system was pumped with a liquid nitrogen trapped Varian VH5-6 oil diffusion pump backed by an Edwards 40 two stage mechanical pump, providing a base pressure of $\sim 6 \times 10^{-7}$ Torr. For all electron beam evaporations, the deposition pressure was $\leq 1-3 \times 10^{-6}$ Torr and the charge consisted of metal pellets with the following purity's: Ni, (Cerac Inc., 99.95%); Au, (Materials Research Corporation, 99.95%); Pd, (AESAR Johnson Matthey Inc., 99.8%); Cr, (Union Carbide, purity unknown), and C, (graphite slug, purity unknown). The metal layer thickness was monitored using a quartz crystal oscillator controlled by a Kurt J. Lesker Company QXM-500 controller. The GaN contact thickness varied with different experiments and will be noted in the results section of Chapter 5.

Following deposition, all metallization schemes were heat treated in the quartz tube furnace previously mentioned using either flowing forming gas or N_2 as the ambient. Separate samples were heated at 200, 400 or 600°C for 5, 15, and 30 minutes. The Ni/Au, Pd/Au and Cr/Au samples were also heated to 900°C for 15 seconds in a 50 cm quartz tube custom rapid thermal annealing (RTA) furnace with a 25 cm hot zone and flowing N_2 as the ambient.

Characterization

Both the p-ZnTe and p-GaN samples were characterized as-deposited and following each of the previously described heat treatments in terms of their electrical properties, and also for their surface composition, surface morphology, and interfacial reaction products as required.

Electrical Characterization

The electrical properties of all contacts were investigated using room temperature current-voltage (I-V) measurements. The I-V data were obtained by measuring the current flow between two adjacent dot contacts under an applied bias. An automated system consisting of an IBM PC with IEEE-488 communications, a Hewlett-Packard 6112 A DC power supply and either a Keithely 488 picoammeter or a Hewlett-Packard 3478A multimeter, depending on the current range measured, was used to obtain the I-V data. A

schematic of this setup is shown in Figure 3.5. The resulting data, collected over a range of -5 to +5 V, was modeled as two back-to-back diode barriers, one forward biased and the other reverse biased, and the ohmic or rectifying nature of the contacts could be determined by the linearity of the I-V curve. The reverse-bias breakdown voltage could also be determined from the I-V characteristics. Barrier heights were also determined from the I-V data, but due to problems involving large ideality factors for the contacts, the calculated barrier heights were concluded to be inaccurate.

The charge transport mechanisms for Ni/Au, Pd/Au, and Cr/Au contacts were determined using temperature dependent I-V measurements. For these measurements, the samples were mounted and Au wire bonded onto TO5 headers which were placed in a liquid nitrogen cooled sample holder. The I-V characteristics were determined from -5 to +5 V using a Hewlett-Packard 6111A DC power supply with a Hewlett-Packard 3455A digital voltmeter and the current was measured across a 1k Ω resistor. The temperature ranged from 80-400 K and was measured using a Pt resistance thermometer calibrated to 0.01° controlled by a Lake Shore Cryogenics DRC 82C temperature controller. All measurements were taken at a pressure of 10 mTorr.

The p-GaN samples were also characterized in terms of their doping character using photoluminescence (PL) [Bru92]

and Hall effect measurements. The PL data was obtained using excitation from a HeCd laser ($\lambda=325$ nm) at a temperature of 22 K for an as-grown sample and also following a 900°C, 15 second RTA in N_2 . For the Hall effect data, In pads were soldered onto the p-GaN and heat treated at 400°C for 3 minutes in N_2 for better adhesion. The data was taken with a current of ± 0.0001 A and a magnetic field of 8 KGs. Following measurement, the In pads were etched using a 10:1 DI:HCl solution and the same sample and contacting process was used following the 900°C heat treatment.

Surface Composition Analysis

Following heat treatment and electrical characterization, the elemental surface composition was determined by Auger electron spectroscopy (AES) [Hol80] using a Perkin-Elmer PHI 660 scanning Auger microprobe (SAM), or by secondary ion mass spectrometry (SIMS) [Ben87] using a Perkin-Elmer PHI 6600. For contacts to p-ZnTe and p-GaN, AES surface survey spectra were recorded over the energy range of 50-2050 eV using a 5 keV, 30 nA electron beam with a diameter of ~ 1 μm . For depth profiles, a 5 keV argon ion beam was used to sputter the sample at a nominal rate of $\sim 100 \text{ \AA/min}$ for 6 second intervals after which the surface was scanned with the electron beam. SIMS depth profiles of Au/p-ZnTe contacts were performed using a 5.5

keV, 53 nA Cs⁺ ion beam with a 200 μm x 200 μm raster size using a quadrupole mass spectrometer to analyze the sputtered ions. For p-GaN, SIMS was performed only on the Ni/C/Au contacts with a 3 or 5 keV, 30 nA Cs⁺ ion beam. The beam had a linear gating of 70% and a 300 μm x 300 μm raster size.

Surface Morphology

Changes in surface morphology were investigated using optical and scanning electron microscopy (SEM) [Gol92]. All samples were viewed following heat treatments with an Olympus BH-2 optical microscope with photographic capabilities for any large changes in surface morphology. SEM was performed on the Au/p-ZnTe samples using a JEOL 6400 scanning microscope with an accelerating voltage of 15 KV.

Interfacial Reaction Products

For Cr/Au contacts on p-GaN, cross-sectional transmission electron microscopy (XTEM) [Edd74] and energy-dispersive x-ray spectroscopy (EDS) [Bru92] were used to determine interfacial reaction products formed in samples subjected to a 900°C, 15 second RTA. These data were compared to as-deposited samples.

For XTEM, the sample preparation technique is extremely important in obtaining high quality samples. For these cross section experiments, two samples were first glued face to face using G1 epoxy (Gatan). This structure was then

placed inside a stainless steel notched rod which was in turn slid into a stainless steel outer tube with an inner diameter just larger than the outer diameter of the rod. GI epoxy was then applied to fix the samples in the notch and to fill the area between the rod and the tube. The epoxy was cured on a hot plate at 100°C for 30 minutes. After curing, samples were cut on a Accutom low speed saw using a diamond blade to a thickness of $\approx 300 \mu\text{m}$. Figure 3.6 shows a planar schematic view of the samples following the cut. The samples were manually polished using SiC polishing paper until one side was smooth, flipped over, and polished down to a thickness of $\sim 100 \mu\text{m}$. A slotted Cu ring was then glued to the sample using M1 epoxy (Micro Measurements Inc.) for added stability. Next the samples were flattened to a thickness of $\sim 30 \mu\text{m}$ on a VCR Group Inc. Dimpler[®] using a tool steel wheel and a 1 mm diameter cylinder. These samples were ion milled in a Gatan Dual Ion Mill (Model 600) with a voltage of 4-6 kV at 1mA with a final milling angle of 12°. After ion milling to produce a hole in the center of the structure, the edges of the hole were electron transparent. The samples were analyzed by amplitude contrast imaging in a JEOL 200CX TEM using a two beam bright field condition. Phase contrast imaging was used to obtain high resolution images in a JEOL 4000FX high resolution TEM. The EDS data was taken with a 400 KeV incident electron beam with a spot size of $\approx 500 \text{\AA}$. Characteristic x-rays were

detected from 1-20 KeV using a Princeton Gamma Tech model
OS26-J029 detector.

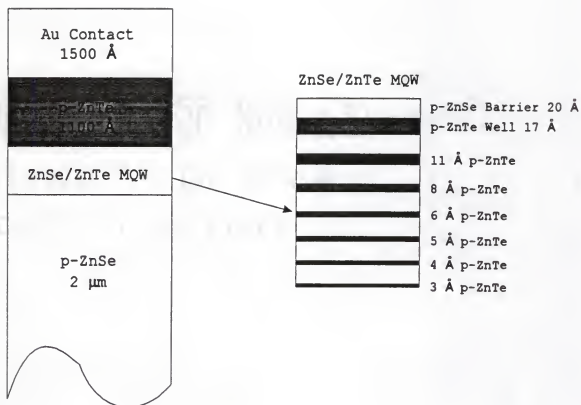


Figure 3.1. Schematic diagram of Au/p-ZnTe sample showing ZnSe/ZnTe MQW.

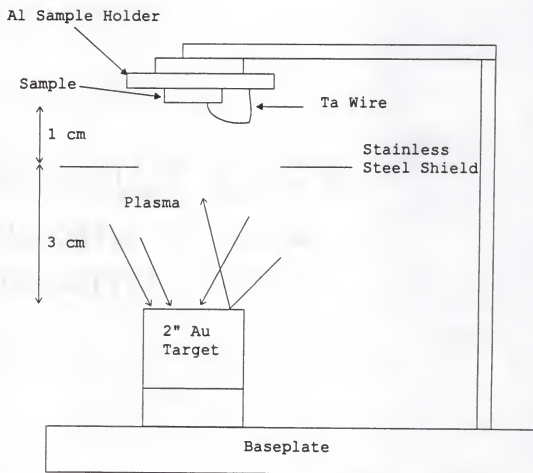
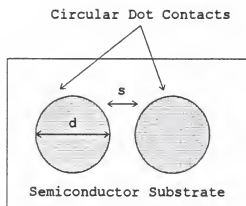
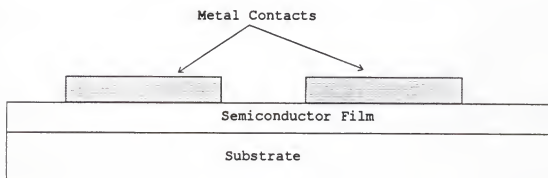


Figure 3.2. Schematic of the sample holder and magnetron source for the sputter system used to deposit Au conacts.



	$\underline{d}$	$\underline{s}$
ZnTe	0.8 mm	0.4 mm
GaN	0.5 mm	0.2 mm

(A) Top View



(B) Side View

Figure 3.3. Top (A) and side (B) views of dot contacts on the semiconductor films showing electrical isolation of the metal contacts.

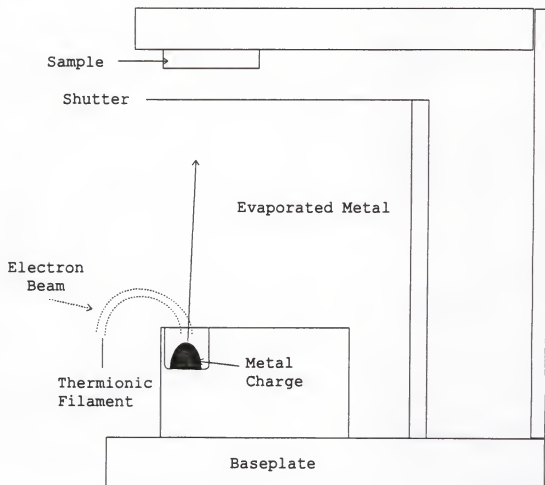


Figure 3.4. Schematic of electron beam evaporation system.

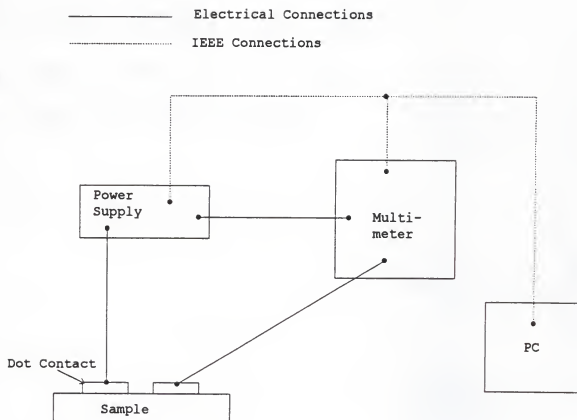


Figure 3.5. Hardware setup for current-voltage measurement system.

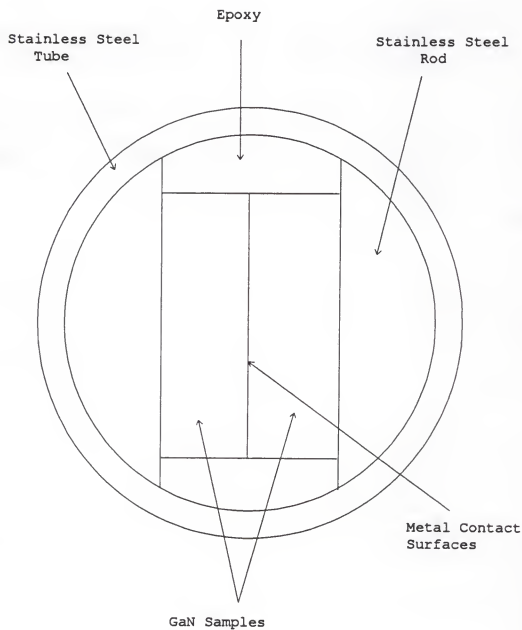


Figure 3.6. Planar view of Cr/Au on p-GaN sample used for XTEM.

CHAPTER 4 p-ZnTe CONTACTS

Introduction

Formation and characterization of Au/p-ZnTe ohmic contacts are discussed in this chapter. The sputter deposited contacts were heat treated in forming gas and current-voltage (I-V) measurements were used to determine the effect of elevated temperatures on the electrical properties. Heat treatments were identified which led to the decrease in contact resistance and formation of the ohmic contacts. The temperature stability of this contact scheme was also studied. Analytical characterization techniques, including Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) depth profiling, were used to identify elemental surface composition, interfacial reactions and compound formation induced by heat treatment. These analytical results, along with surface morphological changes determined from scanning electron microscopy (SEM) were correlated with the electrical results to determine the origin of the ohmic behavior and the eventual degradation of the contact properties.

Results

I-V Results

As-deposited I-V curves were non-linear and characteristic of poor back-to-back Schottky contacts (Figure 4.1). Upon heating to 150°C for 15 minutes, there was a slight reduction in breakdown voltage (V_b) from -0.5 eV to -0.2 V, but the curves remained slightly non-linear. The breakdown voltage was determined by extrapolating the linear region of the I-V curve to its x-axis intercept. For samples heat treated at 200°C and 250°C for 15 minutes, linear I-V curves were measured with decreased contact resistance. A maximum current density of 2.3 A/cm² at 5 V was observed following a 250°C, 15 minute heat treatment. Upon heating at 350°C, the I-V curves remained linear but the resistance was a factor of 25 higher than for samples heated at lower temperatures for equivalent times, indicating degradation of the contacts or increased bulk resistance of the p-ZnTe (Figure 4.2). Increased time at this temperature led to an increased contact resistance. The changes that occurred upon heat treatment of the Au/p-ZnTe contacts are summarized in Figure 4.3 showing that the contacts were thermally stable only for $T \leq 250^\circ\text{C}$.

AES

AES depth profiles were collected for as-deposited samples and after heat treating at 200°, 250°, or 350°C for 90 minutes. The as-deposited profile (Figure 4.4) shows an abrupt Au/p-ZnTe interface indicated by the rapid decrease of the Au signal at ~22 minutes. For samples heat treated at 200° and 250°C (Figures 4.5 and 4.6) the slope of the Au signal versus sputter time was not as large as that of the as-deposited case. The smaller slopes of the Au and Te signals versus depth (at ~11 minutes in Fig. 4.5 and ~9 minutes in Fig. 4.6) indicated that Au had begun to diffuse into the near surface region of the p-ZnTe leading to a slight broadening of the metal/semiconductor interface. Even with this limited diffusion, the interface remained reasonably planar with no evidence of compound formation. In Figure 4.7, the AES depth profile for the 350°C heat treatment would be consistent with an interface between Au and ZnTe which was no longer planar. Au had diffused throughout the ZnTe capping layer and into the underlying ZnSe. The change of Au slope leading to a relatively flat Au signal from ~25-35 minutes of sputtering time suggests formation of an interfacial phase or compound.

SIMS

SIMS depth profiles were measured on samples as-deposited and heat treated at 250° or 350°C for 90 minutes. The as-deposited profile (Figure 4.8) is consistent with a very planar Au/ZnTe interface, similar to the AES depth profile, with no indication of any Au diffusion into the semiconductor. Upon heating at 250°C for 90 minutes (Figure 4.9) Au had begun to diffuse into the ZnTe. At 5 minutes of sputter time the Au signal was larger than the Te signal as opposed to data in Figure 4.8 at -4 minutes of sputter time where the Au signal was less than the Te signal strength and remained lower throughout the profile. At 350°C for 90 minutes (Figure 4.10), it is readily apparent that Au has diffused through the entire ZnTe capping layer and into the underlying ZnSe film.

Surface Morphology

Changes in the surface morphology, which were significant to thermal stability of the Au contacts, were observed. The as-deposited Au film was specular reflective to the eye and very smooth when examined by scanning electron microscopy. After heat treating for 90 minutes at $T < 250^{\circ}\text{C}$ the Au remained specular to the eye. After 250°C for 90 minutes, optical microscopy and SEM showed that the ZnTe between the Au dot contacts became hazy (Figure 4.11). An AES surface survey showed the presence of Au between the

dot contacts, creating an extended diffusion zone $\approx 100\mu\text{m}$ across the ZnTe surface. For the same sample at $t \leq 75$ minutes, $T=250^\circ\text{C}$, there was no evidence of this diffusion. At 350°C for 90 minutes, a rough surface indicative of further degradation was seen (Figure 4.12).

Discussion

Ohmic contacts are characterized by their electrical properties. This section will discuss three changes in the I-V curves upon heat treatment and provide metallurgical explanations for the changes. These changes were: 1) decreased breakdown voltage at 150°C , 2) increased current levels and linear I-V with increased temperature above 150°C , and 3) dramatic resistance increase and contact degradation at 350°C .

To understand the properties expected from Au/p-ZnTe contacts, it must first be determined if the Fermi level is pinned. From the Schottky model for a semiconductor with no Fermi level pinning, Eq. 2.1 predicts the potential offset in the valence band. For Au/p-ZnTe contacts with $E_g=2.26\text{ eV}$ [Mil72], $\chi_{\text{ZnTe}}=3.5\text{ eV}$ [Mil72], and $\phi_{\text{Au}}=5.1\text{ eV}$, Eq. 2.1 yields a value of 0.66 eV . This is in good agreement with the experimentally observed as-deposited value of breakdown voltage $\approx 0.5\text{ eV}$. This would only be expected if the Fermi level was not pinned in p-ZnTe.

The decreased breakdown voltage upon heat treating to 150°C for 15 minutes is attributed to decomposition of the thin interfacial contamination layer, evident from the weak oxygen signal in Figures 4.4-4.7. The increased current and linear I-V curves after heating to 200°C are attributed to diffusion of Au into the underlying ZnTe. The analytical results from the AES depth profiles (Fig. 4.5 and 4.6) show a broadening of the Au/ZnTe interface consistent with Au diffusion into the near-surface region of the p-ZnTe. The SIMS depth profile for 250°C (Fig. 4.9) also shows direct evidence of Au diffusion into the ZnTe capping layer. Au has been shown to be principally accommodated substitutionally on Zn sites (Au_{Zn}) and to form a simple acceptor level at E_v+272 meV. [Mag80] Thus it is proposed that the introduction of Au as an acceptor species in ZnTe was responsible for the increased current after elevated temperature treatments and therefore the ohmic contact.

If Au was acting as an acceptor in p-ZnTe and increased the doping concentration of the near-surface region, the main conduction mechanism in these Au/p-ZnTe contacts should have been field emission. To evaluate whether field emission or thermionic emission was dominant, thermionic emission currents were modeled using Eq. 2.5-2.8. For these calculations, the following values were used; Φ_b for Au on p-ZnTe = 0.73 eV, $T = 300$ K, $area = 0.005$ cm² (0.8 mm diameter), $N_A = 3 \times 10^{18}$ cm⁻³, hole effective mass = 0.60, and low frequency

dielectric constant $\epsilon=9.4$. [Wag92] The built in potential of the junction (V_i) was calculated by determining the position of the Fermi level and subtracting this value from Φ_B . Based on these calculations, the reverse bias breakdown voltage for the Au/p-ZnTe contacts would be 18 V if thermionic emission was dominant, rather than the observed value of 0.5 eV. Thus thermionic emission was not dominating current transport.

Therefore the properties of the Au/p-ZnTe contacts were modeled based on field emission. From the equations for field emission, taking the natural logarithm of Eq. 2.11 and with some simple rearrangements:

$$\ln(I) = \ln(I_s) + (-qV_R/E_o). \quad (4.1)$$

Based on this equation, a plot of the $\ln(I)$ vs. V should produce a straight line if tunneling is dominant. Figure 4.13 shows a plot of $\ln(I)$ vs. V from 0-5 volts for an as-deposited sample as well as samples heat treated at 150, 200, 250, or 350°C for 15 minutes. As can be seen in all cases, the plot of $\ln(I)$ vs. V was only linear for $V \geq 2V$, indicating that tunneling was not dominant over the entire range of reverse biases.

The barrier height for the metal/semiconductor contacts can also be determined from the plot of $\ln(I)$ vs V . From these curves the value of the saturation current I_s can be obtained by extrapolating the linear portion of the curve to $V=0$. Knowing I_s , Richardson's constant A , the diode cross

sectional area S , and the temperature T , the barrier height (Φ_b) can then be determined from:

$$I_0 = SAT^2 \exp(-\Phi_b/kT). \quad (4.2)$$

The value of barrier height obtained in this way is the zero bias barrier height and includes the image force barrier lowering $\Delta\Phi_b$. The values of Φ_b for Au/p-ZnTe contacts are shown in Table 4.1. However, when the diode ideality

Table 4.1. Barrier heights for Au/p-ZnTe contacts.

Heat Treatment	Φ_b (eV)
As-deposited	0.433
150°C, 15 min	0.426
200°C, 15 min	0.419
250°C, 15 min	0.412
350°C, 15 min	0.504

factor, n , was determined from the following equation:

$$I = I_0 [\exp(qV/nkT) - 1], \quad (4.3)$$

values of $n=100$ were obtained which violated the initial assumption of the analysis. Therefore this reduction of I - V data to Φ_b is erroneous and will not be continued.

With neither thermionic nor field emission dominating conduction over the voltage range from 0-3 V, it is proposed that thermionic field emission is the dominant mechanism. Thermionic field emission is an intermediate conduction mechanism which combines both thermionic and field emission processes. In a case where the barrier height is too large for thermionic emission to take place and the depletion

width is too deep for tunneling to occur, current can be transported by the thermal excitation of holes to a level at which the potential barrier is thin enough for tunneling to occur. This process is known as thermionic field emission and it dominates for mid-range temperatures and moderate doping concentrations. In Chapter 2, the tunneling parameter E_0 was introduced as a measure of the relative importance of thermionic versus field emission transport. From Equation 2.13 for Au/p-ZnTe, E_0 is 0.0135 eV. This value is approximately the room temperature value of kT (0.0258 eV) which indicates thermionic field emission should dominate conduction. While this value of E_0 is smaller than kT , increasing the near-surface carrier concentration by Au diffusion would cause the value of E_0 to approach kT . The non-linearity of the $\ln(I)$ vs V plots at $V < 3V$ would discount pure field emission.

TFE dominance is also supported by the fact that Au is a relatively deep acceptor in ZnTe (272 meV). This level is too deep for the acceptors to be sufficiently activated at room temperature, leading to the non-linear I-V curve for as-deposited samples. Upon heat treatment of the Au/p-ZnTe contacts, increased Au diffused into the p-ZnTe would in turn increase the carrier concentration. The Au atoms then can participate in conductivity through the process known as hopping conduction. [Mil73] In this process, a charge carrier, in this case a hole, can move from one deep defect

center to another by the tunnel effect without activation into the valence band. This method of conductivity is common where there is a high density of these centers with no alternative transport mechanism [Mark95].

Based on the AES and SIMS depth profile data, no compounds formed at $T \leq 250^\circ\text{C}$ which could have affected current transport, which lends support to the Au doping postulate. Surface conductivity played no role in the I-V data measured for the contacts heat treated for 15 minutes. The surface diffusion, evident in Figure 4.11, occurred upon heating for extended times (90 minutes) and thus had an insignificant role in the I-V data measured after 15 minutes when no visible surface diffusion was present.

The final change in the I-V curves for Au/p-ZnTe upon heat treating was the dramatic increase in resistance upon heating to 350°C . As was shown in the I-V curves of Figure 4.3, the current passed following a 350°C heat treatment was approximately two orders of magnitude lower than for the contacts heat treated at lower temperatures. It was also shown that increased heat treatment time at this elevated temperature caused an increased resistance. It is proposed that widespread diffusion of Au along with interfacial phase formation, as evidenced from AES and SIMS depth profiles, limited the temperature stability of these contacts.

Au and Te form a congruently melting compound AuTe_2 [Mas90] which is postulated to be responsible for the

contact degradation in these Au/p-ZnTe samples. It is suggested that this AuTe₂ phase is forming at the expense of the ZnTe layer, causing increased resistance. As mentioned previously, Au may be substitutionally incorporated into the ZnTe lattice on a Zn site. With increased time at this elevated temperature, more Au can be incorporated into the ZnTe until a point at which AuTe₂ forms in place of the ZnTe. It is this total breakdown of the ZnTe, caused by Au diffusion and formation of AuTe₂, which is postulated to be responsible for the degraded contact performance at 350°C. The I-V curves in Figure 4.2 show that as the heat treatment time at 350°C was increased, more degradation occurred which supports this postulate since diffusion is both time and temperature dependent.

Summary

Formation of ohmic contacts to nitrogen doped p-ZnTe by sputter deposition of Au films was demonstrated. As-deposited contacts were rectifying with a breakdown voltage of ≈ 0.5 eV, close to the barrier height value of 0.66 eV obtained from the band alignment. This strongly suggests that the Fermi level was not pinned in ZnTe. Slightly decreased breakdown voltages after heat treatments at 150°C were attributed to the breakup of interfacial contamination layers. Heating for 15 minutes at $T \geq 200^\circ\text{C}$ resulted in ohmic

behavior which was credited to creation of near-surface acceptors due to doping by Au without interfacial phase formation. This led to increased conductivity through the near-surface layer, culminating in a maximum current density of 2.3 A/cm^2 at 5 V following 15 minutes at 250°C . This increased conduction was attributed to thermionic field emission occurring in the contacts at $V < 3\text{V}$, and field emission for $V > 3\text{V}$. Au acceptors with an energy of $E_v + 272 \text{ meV}$ were proposed to participate in current transport by hopping conductivity between deep centers in the lattice. Diffusion of Au was extensive and resulted in AuTe_2 compound formation at 350°C , leading to severe degradation of the contact properties.

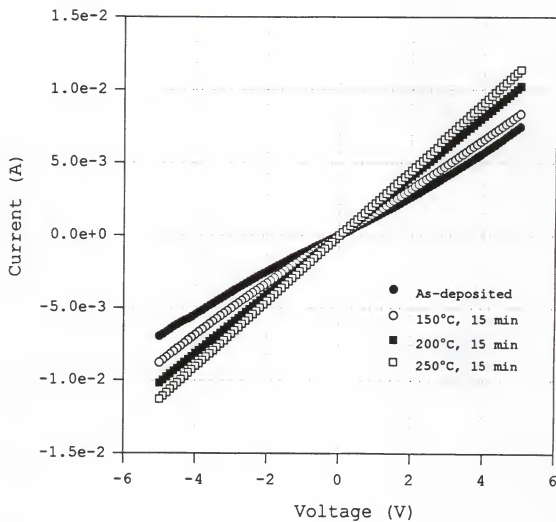


Figure 4.1. I-V curves for Au/p-ZnTe.

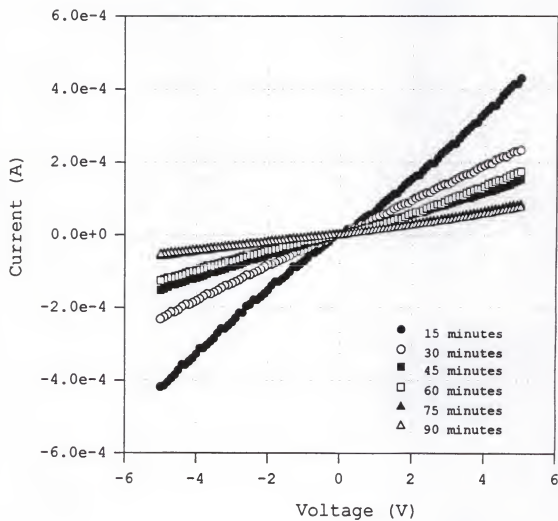


Figure 4.2. I-V curves for Au/p-ZnTe heat treated at 350°C in forming gas.

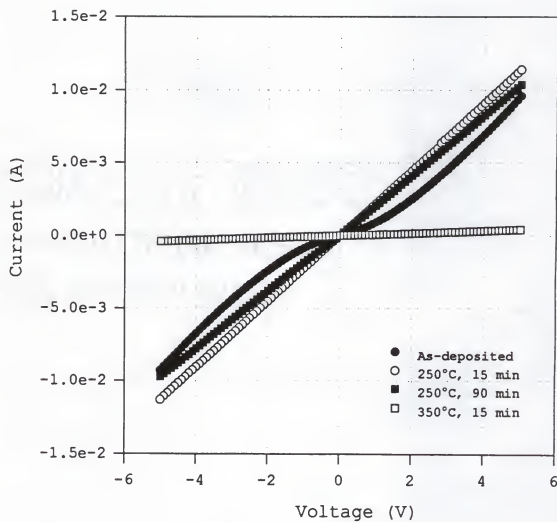


Figure 4.3. I-V curves for Au/p-ZnTe.

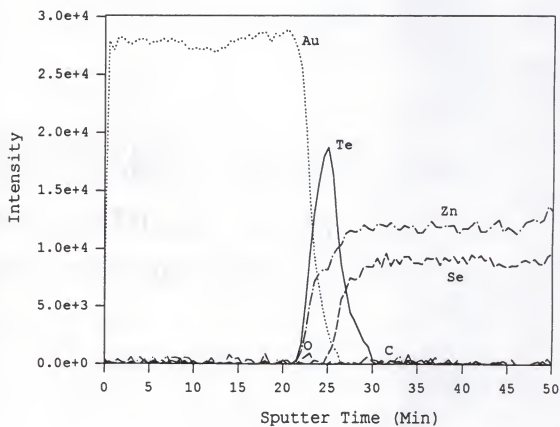


Figure 4.4. AES depth profile of Au/p-ZnTe, as-deposited.

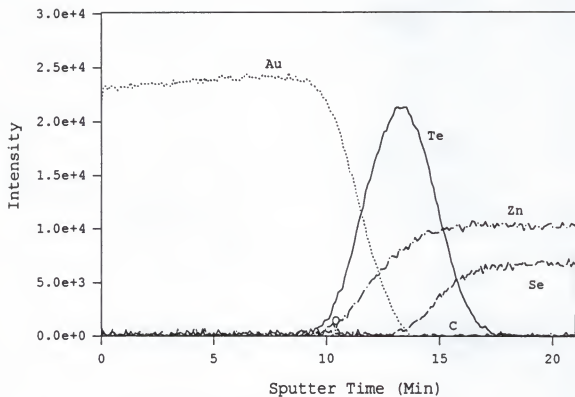


Figure 4.5. AES depth profile for Au/p-ZnTe sample heat treated at 200°C for 90 minutes.

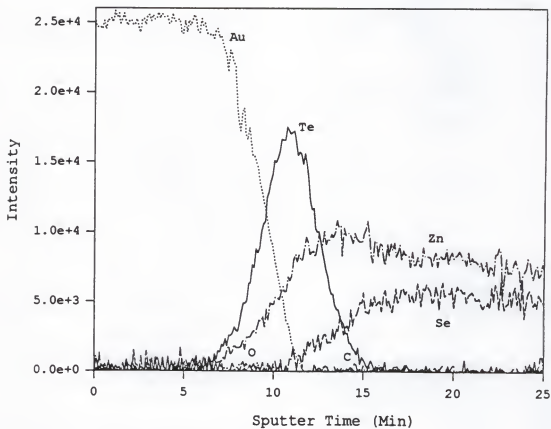


Figure 4.6. AES depth profile for Au/p-ZnTe sample heat treated at 250°C for 90 minutes.

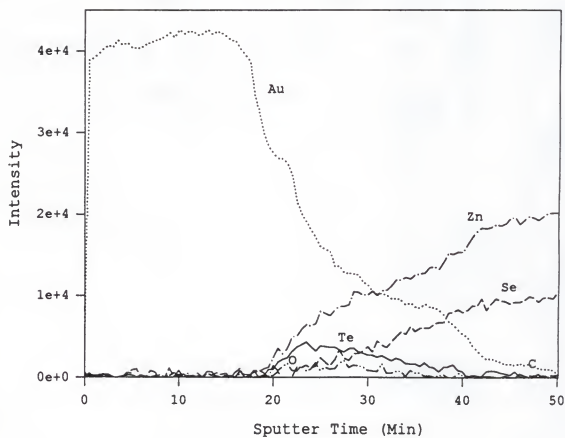


Figure 4.7. AES depth profile for Au/p-ZnTe sample heat treated at 350°C for 90 minutes.

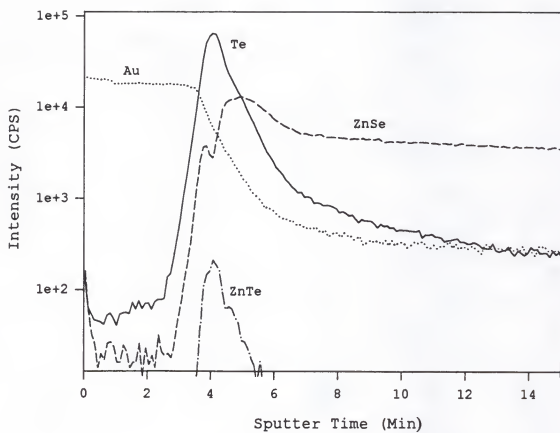


Figure 4.8. SIMS depth profile for Au/p-ZnTe sample, as-deposited.

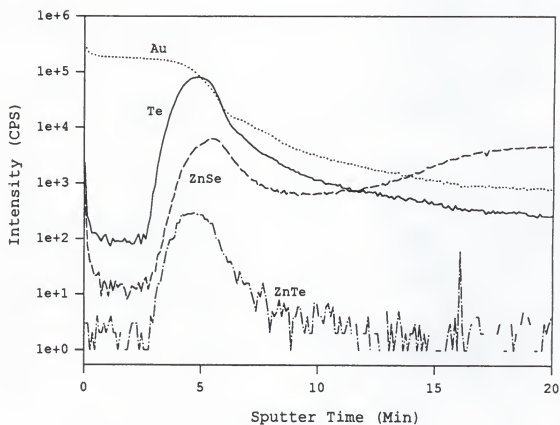


Figure 4.9. SIMS depth profile for Au/p-ZnTe sample heat treated at 250°C for 90 minutes.

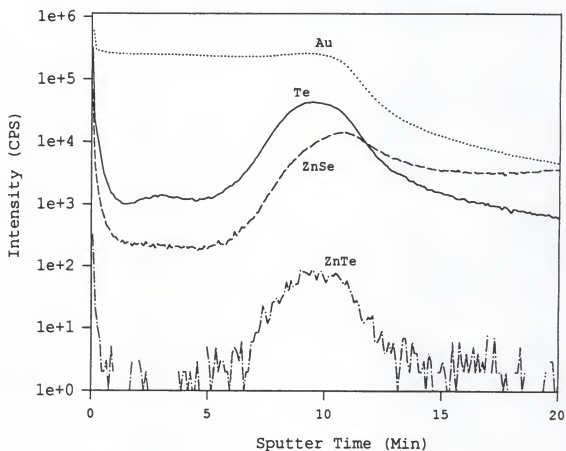


Figure 4.10. SIMS depth profile for Au/p-ZnTe sample heat treated at 350°C for 90 minutes.

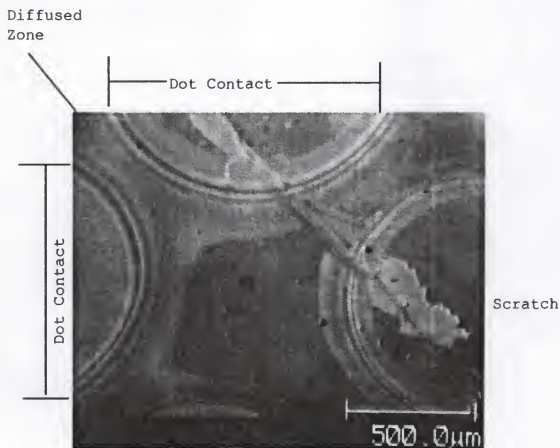


Figure 4.11. SEM micrograph of Au/p-ZnTe sample heat treated at 250°C for 90 minutes showing an extended reaction zone surrounding the Au contact.

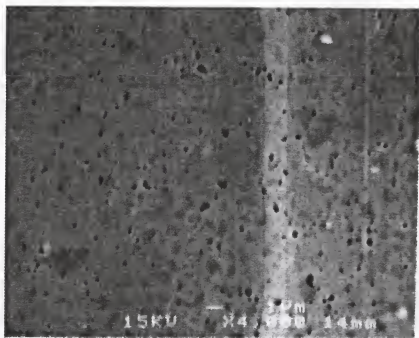


Figure 4.12. SEM micrograph of the surface of a Au dot on a Au/p-ZnTe sample heat treated at 350°C for 90 minutes showing roughening of the Au contact.

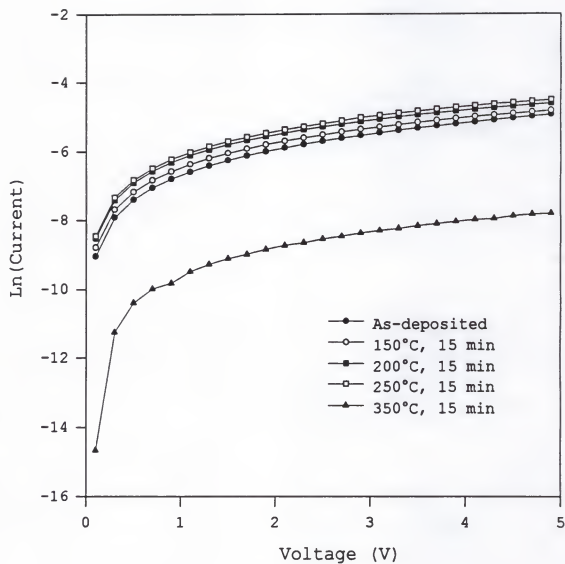


Figure 4.13. Plot of $\ln(I)$ vs. V for Au/p-ZnTe.

CHAPTER 5 p-GaN CONTACTS

Introduction

The formation and characterization of electrical contacts to p-GaN are described below. The contact metallizations consisted of a single element (Au), bi-layer contacts (Pd/Au, Ni/Au, and Cr/Au), and a three layer contact scheme (Ni/C/Au). The elements are listed in the order in which they were deposited, i.e. the first element was deposited on GaN. As for Au/p-ZnTe contacts discussed in Chapter 4, the effects of elevated temperature treatments for various times on the electrical properties of the p-GaN contacts were determined using I-V measurements. Analytical characterization of the contacts included AES and SIMS depth profiles, along with energy-dispersive x-ray spectroscopy (EDS) and cross-sectional transmission electron microscopy (XTEM) to determine composition and interfacial reaction products. Photoluminescence (PL) and Hall measurements were also used to determine doping character of the material. Temperature dependent I-V data were used to determine the dominant conduction mechanisms for the Ni/Au, Pd/Au and Cr/Au contacts. In this chapter the results from I-V

measurements, analytical characterization, and temperature dependent I-V are given for all metal contacts, followed by a discussion of these results. Finally, the results are summarized.

Results

Au

I-V results

Au contacts (2000Å) were sputter deposited onto p-GaN which had a resistivity of 7 Ωcm and a free hole concentration $N_A = 1 \times 10^{17} \text{ cm}^{-3}$. As deposited the I-V curves were rectifying with a breakdown voltage of $\approx 2.5 \text{ V}$ (Figure 5.1). The barrier height (Φ_b) was calculated using the method described in chapter 4 to be 0.62 eV, but again the ideality factor was ≈ 100 , therefore no further Φ_b data will be reported. Instead only the breakdown voltage will be determined using the procedure described earlier. When this same sample was heat treated at 400°C for 5 minutes in forming gas, the breakdown voltage was reduced to $\approx 0.8 \text{ V}$. After 600°C for 15 minutes, the breakdown voltage decreased only to $\approx 1.5 \text{ V}$. The I-V curves remained rectifying for all heat treatments.

AES

The Au and Ga signals in AES depth profiles from contacts as-deposited or heat treated at 400°C for 15

minutes in forming gas can be seen in Figure 5.2. For the as-deposited sample, there is a very sharp interface between the Au and GaN with no indication of GaN decomposition. At 400°C for 15 minutes, the slope of the Au signal is identical to that of the as-deposited profile. The interface is still planar with no evidence of GaN decomposition or Au diffusion into the GaN matrix to the level detectable by AES.

Pd/Au

I-V results

Contacts of Pd/Au (500/1000Å) on p-GaN ($N_A=9.8 \times 10^{16} \text{ cm}^{-3}$) were also studied. For as-deposited contacts, the I-V curves were rectifying (Figure 5.3) with a breakdown voltage of $\approx 3 \text{ V}$. Heating at 200°C for 5 minutes in flowing N_2 caused the contacts to become more rectifying and pass less current with an increased breakdown voltage. The I-V curves were unchanged by increasing the time at 200°C up to 30 minutes. After 400°C for 5 minutes, the current was slightly greater than for as-deposited samples. Heating for times up to 45 minutes at 400°C led to a 60% increase in current and a reduction in breakdown voltage from 2 to 1.5 V. The I-V data from samples annealed at 600°C for 5 minutes were similar to those after 400°C for 45 minutes. After an RTA at 900°C for 15 seconds in N_2 , the contacts

were

still rectifying, but the breakdown voltage was decreased to ≈ 1 V with 5 mA of current at 5 V.

AES

As-deposited (Figure 5.4), the Au/Pd interface was broadened and at the Pd/GaN interface there was a slight Pd tail into the GaN, but no evidence of Ga out-diffusion into the overlaying films following deposition. At 200°C for 5 minutes (Figure 5.5) there was an increased broadening of the Au/Pd interface with a small Pd signal continuous throughout the Au layer to the surface. The AES survey spectrum (Figure 5.6) showed a Pd transition at 327 eV, indicating that Pd diffused through the Au layer. The Pd signal also tailed into the GaN, but there was no evidence of Ga out-diffusion. After 400°C for 5 minutes (Figure 5.7), Pd continued to diffuse through the Au capping layer, but did not build up at the surface. Thus there were constant levels of Pd and Au throughout the first layer, followed by a Pd-rich layer underneath. The Pd/GaN interface has broadened, but there was still no evidence of dissociation of the GaN. In Figure 5.8, the AES depth profile after an RTA of 900°C, 15 seconds shows that Pd had completely dissolved into the Au layer forming a Au:Pd region contacting the underlying GaN. The depth profile suggests that dissociation of GaN occurred because a Ga signal was detected throughout the contact layer up to the surface. The long Pd and Au tails into the GaN suggest

diffusion into the GaN. Following this RTA heat treatment, the contacts exhibited both dark regions rich in Pd and Au (Figure 5.9), and light regions rich in Pd, Au, Ga, and N (Figure 5.10).

Ni/Au

I-V results

Evaporated Ni capped with sputtered Au (500/2400Å) contacts deposited on the same substrate as the Au contacts were rectifying as-deposited with a lower breakdown voltage (≈ 0.5 V) and larger current (≈ 0.5 mA @ 5 V) than the Au/p-GaN contacts (Figure 5.11). The I-V curves remained rectifying up to 200°C, but after a 400°C, 5 minute treatment, they became nearly linear with ≈ 0.6 mA passed at 5 V. Upon heating this sample to 600°C for 5 minutes, the contacts degraded as reflected by lower current levels (Figure 5.11).

The effects of Ni layer thickness and Ni to Au thickness ratios are shown in Figure 5.12. Data are shown from as-deposited and heat treated (400°C, 5 min. in forming gas) samples ($\rho = 17$ Ω cm) with evaporated 200/2000Å or 500/1000Å Ni/Au contacts. The as-deposited samples were very similar in both current magnitude (0.1 mA @ 5 V) and breakdown voltage (≈ 2.2 V). After heat treatment, the breakdown voltage was drastically reduced to ≈ 0.5 V even though the I-V curves remained slightly rectifying. There

was very little difference in the I-V data for different metal thicknesses and thickness ratios after the heat treatment.

The effects of heat treatment ambient were also investigated for Ni/Au contacts. Initial heat treatments were performed in a forming gas environment, but this was changed to N_2 due to reports of hydrogen passivating Mg acceptors in p-GaN [Pea96a]. Use of N_2 also reduced the probability of N vacancy formation in GaN which may lead to semi-insulating films. The difference in current levels obtained was negligible between the different ambients, but it was determined that N_2 were preferable to prevent any potential acceptor passivation, especially at elevated temperatures.

AES

An AES depth profile for an (500/1000 Å) contact can be seen in Figure 5.13. There is a planar Ni/Au interface with no indication of intermixing upon deposition. The Ni/GaN interface appears less sharp with a slight Ni tail into the GaN indicative of near-surface diffusion, but this could result from loss of resolution at greater sputter depths [Hol81]. There is, therefore, no evidence of GaN dissociation upon deposition except for the rather low breakdown voltage for as-deposited films. The depth profile for a sample heated to 200°C for 5 minutes in flowing N_2 was similar to the as-deposited profile. After 400°C for 5

minutes (Figure 5.14) the Ni/GaN interface was slightly more diffuse, and Ni diffused through the Au capping layer to the surface of the contact. For heat treatments of 600°C (Figure 5.15), dramatic evidence of GaN dissociation is obvious. Ga was detected at the Au/ambient surface, however Ni also diffused through the Au capping layer to the surface and formed a NiO_x layer. There was also an increased C signal at the metal/p-GaN interface.

Ni/C/Au

I-V results

As will be discussed, the increased current for heat treated Ni/Au contacts could have resulted from C doping of the GaN surface. Therefore, the next contact scheme investigated was an evaporated carbon layer intermediate between the Ni and Au layers to give a Ni/C/Au contact (500/100/1000Å) on p-GaN with a carrier concentration of $2 \times 10^{17} \text{ cm}^{-3}$. I-V data for the Ni/C/Au contacts were rectifying as-deposited and remained rectifying with all heat treatments up to 400°C for 5 minutes (Figure 5.16). The contacts exhibited a decrease in current vs. voltage upon heating to 200°C for 5 minutes. This was then followed by increased current at 400°C for 5 minutes. For all heat treatment conditions, the currents were lower and the potential offsets higher than in the Ni/Au contacts under similar processing conditions.

AES and SIMS

The AES depth profile from an as-deposited Ni/C/Au contact (Figure 5.17) showed more diffuse Au/C, C/Ni and Ni/GaN interfaces than for a Au/Ni contact. The peak of the carbon signal occurred before the Au signal had decreased to zero and there was a very long C tail into the Ni layer. The Ni/GaN interface was also very broad. The depth profile after heat treatment at 400°C for 30 minutes (Figure 5.18) was similar to the as-deposited profile with no evidence of Ni diffusion to the surface or of GaN dissociation.

In the SIMS depth profiles, there were well defined interfaces between all layers in an as-deposited sample (Figure 5.19) with a noticeable C tail into the Ni region of the sample. After heating to 400°C for 30 minutes in forming gas (Figure 5.20), the interfaces were less well defined and the C signal at the Au/Ni interface broadened. As in the Ni/Au contacts, there was evidence of Ni diffusion through the Au contact to the surface and the Ni signal tailed into the p-GaN substrate with no evidence of Ga at the ambient/Au surface.

Cr/Au

I-V results

I-V results from as-deposited Cr/Au (500/1000Å) contacts were once again rectifying, but with a breakdown voltage ≈ 1 -1.5 V (Figure 5.21). Annealing at 200°C for 5

minutes in flowing N_2 resulted in rectifying contacts with lower transported current, similar to the other contact schemes. At $400^\circ C$ for 5 minutes, the breakdown voltage was ~ 1 V. Following an RTA at $900^\circ C$ for 15 seconds, the I-V curves were linear with ~ 13 mA @ 5 V. For this sample an upper limit on the specific contact resistance has been calculated to be $\leq 4.3 \times 10^{-1} \text{ } \Omega \text{cm}^2$ by assuming a bulk resistance of zero for the underlying p-GaN.

AES

In the as-deposited AES depth profile (Figure 5.22), the Cr/Au interface was sharp while the Cr/GaN interface showed a Cr tail into the GaN, but no evidence of dissociation of GaN. In contrast to the AES data from the other metallization schemes, there were small but detectable carbon concentrations at the Cr/Au and Cr/GaN interfaces. After $200^\circ C$ for 5 minutes in N_2 (Figure 5.23), the depth profile was similar in all aspects to the as-deposited profile. At $400^\circ C$ for 5 minutes, Cr diffused through the Au capping layer to the surface and formed an oxide layer similar to the Ni reaction observed in the Ni/Au contacts (Figure 5.24 vs Figure 5.14). Following this heat treatment, an increased C signal was only detected at the Cr/GaN interface. After a $900^\circ C$, 15 second RTA (Figure 5.25), there was massive Cr diffusion through the Au capping layer to the surface and also into the GaN layer. GaN dissociation was evident from the large Ga signal in the Au

region (~8-15 minutes sputter time) without a corresponding N signal and the small Ga signal at the surface. There were increased Cr, nearly constant N and reduced Ga signals in the region of the original Cr layer.

XTEM and EDS

XTEM and EDS were performed on as-deposited Cr/Au contacts and following the 900°C, 15 sec RTA anneal. For the as-deposited sample, the micrograph in Figure 5.26 shows a low magnification (x 73K) image of the contact/GaN structure. The polycrystalline Au and Cr metal layers are fairly uniform in thickness across the contact. In this figure the appearance of the Au layer being $<1000\text{\AA}$ thick is attributed to the ion milling process which removed part of the Au capping layer. The ring structure of the selected area diffraction pattern (SADP) in Figure 5.27 is indicative of polycrystalline material with rings from both Au and Cr observed as shown. EDS data (Figure 5.28) were consistent with discrete metal layers. After the RTA anneal, the metal/GaN interface was no longer planar as shown by Figure 5.29. In the thicker regions of the metal contact in Figure 5.29, EDS spectra (Figure 5.30) show the presence of both Au and Cr. While exact compositions can not be obtained from this data, the relative intensities of the Au and Cr peaks can be used to ascertain that Cr has diffused through the Au capping layer and there are regions where both Au and Cr are present which is consistent with intermixing. This Cr

diffusion is also supported by the depth profile (Figure 5.25).

In Figure 5.31 a high resolution XTEM of the ambient/contact surface is shown. The presence of Ga at this surface, as determined by EDS (Figure 5.32), indicated Ga out-diffusion from the GaN and segregation to the surface. SADP's taken from the regions indicated in Figure 5.31 show a polycrystalline phase containing Au and Cr (Figure 5.33), and a multi-crystal phase which includes Ga along with Au and Cr (Figure 5.34).

Temperature Dependent I-V

Temperature dependent I-V measurements were used to determine the conduction mechanisms dominating in the Ni/Au, Pd/Au and Cr/Au contacts. The I-V data for a Ni/Au (500/2500Å) sample heated to 600°C (873K) for 5 minutes in flowing N₂ are shown in Figure 5.35. The contacts were rectifying at all temperatures between 80-400 K. The current increased and the reverse bias breakdown voltage decreased with increasing temperature.

The temperature dependent I-V data for a Pd/Au (500/1000Å) sample heated to 600°C (873K) for 15 minutes in flowing N₂ are shown in Figure 5.36 for temperatures 90-390 K. As for Ni/Au contacts, the current increased and the reverse bias breakdown voltages decreased with increasing temperature. The current increase was much more dramatic

for Pd/Au versus Ni/Au contacts, but all contacts remained rectifying.

For Cr/Au (500/2500Å) contacts annealed at 400°C (673K) for 5 minutes in flowing N₂, the 80-400 K temperature dependent I-V data can be seen in Figure 5.37. The I-V curves were slightly rectifying at all measurement temperatures. Unlike Pd/Au and Ni/Au contacts, there was very little increase in current with increased temperature. The reverse bias breakdown voltage also remained nearly steady over this temperature range.

Discussion

Metal Contact Schemes

As previously mentioned in Chapter 1, GaN has a direct band gap of 3.4 eV and an electron affinity between 3.3-4.1 eV. Plugging these values into Equation 2.1 to find the potential offset in the absence of Fermi level pinning leads to values of 6.7-7.5 eV required for metal work functions to decrease the potential offset at the semiconductor valence band to zero. This becomes important due to the fact that metal work functions do not have values greater than ≈ 5.5 eV [Sze81]. Thus in the absence of interfacial reactions, there will always be a potential offset between metals and p-GaN. Because of this, the interfacial reactions between the metal contacts and p-GaN upon heat treatment are of

utmost importance for formation of low resistance ohmic contacts.

Thus there was a need to discover a metal contact scheme that would react with the underlying GaN either as-deposited or upon heat treatment to form ohmic contacts. These metal schemes could provide low resistance contacts in one of two ways. First, the formation of a large work function compound or phase would decrease the potential offset at the valence band, and second the doping concentration in the near-surface region of the semiconductor could be increased by incorporation of acceptor dopant species from either the contact layer or interfacial contamination.

Au

The work function of Au is 5.1 eV [Sze81], so the calculation reported above predicted that the as-deposited contacts would be rectifying, as was the case. Au has been reported to exhibit limited reaction with GaAs as a single element contact and increased reactivity upon incorporation in a contact scheme such as Au/Ge/Ni or Au/Zn [Bras83]. The ohmic behavior is then observed through a solid state regrowth process in the manner described by Sands et al. [San88], and Holloway et al. [Hol97]. As seen in Figure 5.2 for the Au/GaN contacts, there was no evidence of Au:Ga phase formation upon deposition or following heating at 400°C. Thus Au on GaN is non-reactive, leading to the

conclusion that the presence of additional metals in the contact scheme is required for ohmic contact formation.

Pd/Au

With no discernible Au/GaN reaction evident upon heat treatment, interfacial metal layers were introduced into the contact scheme to induce reaction with GaN. For Pd/Au contacts (500/1000Å) interfacial reactions played extremely important, complex roles in interface transport. As reported above, there was evidence of a small uniform amount of Pd throughout the Au contact layer after heating to 200°C, but surface segregation was not observed. Upon heating at 400°C for 5 minutes, diffusion continued until a signal intensity ratio of ~2:1 Au:Pd formed at the surface, as can be seen in Figure 5.7. The I-V data showed higher current levels and lower breakdown voltages at 400°C. It is proposed that as a result of the heat treatment there was interface dissociation and breakup of the interfacial oxide on GaN which led to increased conduction across the contacts. This is consistent with reports that Pd will dramatically dissolve adsorbed C and O. This reaction continued with increased heat treatment time at 400°C, leading to lower contact resistances. This reaction is presumed to be completed at 600°C since longer times at this temperature did not lead to increased conduction. Upon an RTA heating to 900°C for 15 sec, the current levels increased to their greatest values and this increase was

accompanied by dissociation of the GaN as evidenced by the increased Ga signal throughout the entire Au:Pd contact region.

Thus, the breakdown of the interfacial oxide and contamination caused by the dissolving of C and O in the Pd layer is believed to be responsible for the increased conduction upon annealing at temperatures between 400° and 600°C. It is speculated that upon heating to 900°C, dissociation of GaN occurred allowing increased doping of the near-surface region, possibly by Pd acceptors or interfacial C contamination. At lower temperatures, with no GaN dissociation, a lower Ga vacancy concentration decreased the probability for acceptor species to incorporate substitutionally in the GaN lattice. Thus while Pd aids in the dissociation of the interfacial oxide, it may lessen the effects of C doping of the near-surface region and does not lead to an ohmic contact.

Ni/Au

The next contact scheme investigated included an interfacial Ni layer to induce reaction with GaN leading to increased doping. This is the contact scheme presently used in experimental laser diodes [Nak97]. Bermudez et al. have deposited Ni layers on atomically clean GaN and investigated the reactions [Ber93]. They determined that chemical reaction at the interface between GaN and Ni occurred even near room temperature, and annealing above =600°C led to a

pronounced interfacial reaction with the appearance of Ga at the Ni surface. They also determined that the Ga remained dissolved in the Ni layer rather than forming a stable compound or surface segregated layer.

In this study, Ni ($\Phi_{Ni}=5.15$ eV) formed a rectifying contact as-deposited with a breakdown voltage of 0.5-0.6 eV. This value is lower than that predicted from the energy band alignment (1.55 eV) for a clean GaN surface with no Fermi level pinning which would be consistent with undetected dissociation of GaN upon deposition. In the AES depth profile from an as-deposited contact (Figure 5.13), the slight Ni tail into the GaN is consistent with Ni diffusion into the semiconductor during deposition, as suggested by Bermudez et al. [Ber93]. With heat treatment to 400°C, there was evidence of Ni diffusion through the Au capping layer to form NiO_x at the surface.

At 600°C for 30 minutes, the AES depth profile (Figure 5.7) showed direct evidence of GaN dissociation upon heat treatment. Dissociation of the GaN was evident from the fact that Ga diffused through the Ni/Au contact layer and piled up at the surface. The Ni and Au interdiffused and the width of the Ni/GaN interface increased significantly, consistent with widespread diffusion of Ni into the GaN lattice or roughening of the Ni/GaN interface. The reaction products of dissociation of GaN by Ni are uncertain, since there is a low solubility of N in Ni even though Ni will

combine with Ga to form a solid solution and several binary intermetallic phases [Mas90]. Unfortunately, simple dissociation of the GaN lattice should not result in ohmic contacts without an increased carrier concentration in the near surface GaN region. There are two potential acceptors in this system since Ni has been shown to be a deep acceptor in GaAs [Mil73], thus the possibility exists that Ni will behave similarly in GaN. Carbon from interfacial contamination may have incorporated into the GaN lattice during this interfacial reaction, and Abernathy et al. [Abe95] have shown that C can act as an acceptor in GaN. Carbon was found to form a shallow acceptor with a binding energy of ~ 0.2 eV while sitting on the nitrogen sublattice [Fis95], therefore it is reasonable to speculate that interfacial contamination detected by both AES and SIMS could lead to a higher free hole concentration at the interface. It has been calculated that in order to obtain field emission in these Ni/Au on p-GaN contacts, a doping density of $\sim 2 \times 10^{19} \text{ cm}^{-3}$ would be required. Thus the combination of interfacial C and possibly Ni acceptors could provide the needed carriers for ohmic contacts to form. In summary, diffusion and intermixing of Au and Ni occurred upon heating to 400°C , with extensive dissociation of GaN at 600°C , and thus led to improved contact properties.

Ni/C/Au

Contacts of Ni/C/Au, with 100Å of evaporated C were tested to determine if increased doping and better ohmic contacts would be observed with the intentional presence of C. As shown in Figure 5.8, this contact scheme exhibited a higher resistance than did the Ni/Au scheme under all heat treatment conditions. Additional evaporated C at the metal/semiconductor interface did not improve the contact behavior. This could result from a number of factors, including that the concentration of interfacial C contamination was sufficient to saturate the acceptor doping effects and the additional evaporated C layer led to self-compensation of carbon acceptors (C_N) by carbon donors (C_{Ga}). In addition, interfacial contaminating carbon is largely "adventitious" organic and hydrocarbon molecules which are similar to the C source used by Abernathy et al. [Abe95] to demonstrate p-doping of GaN. Evaporated C in a thin film is bound primarily in a ring structure, which is notoriously poor as a doping source during thin film growth.

Cr/Au

With regard to Cr/Au (500/1000Å) contacts, Cr has a smaller work function ($\Phi_{Cr}=4.5$ eV) than the other metals investigated, so there is a greater need for interface reactions. As with all bi-metal contacts, the two important interfaces are Cr/GaN and Cr/Au. As-deposited XTEM (Figure 5.26) showed uniform metal layer thickness across the

contact, and the AES depth profile (Figure 5.22) showed an abrupt Cr/Au interface. However, the Cr/GaN interface was broadened with an elevated C level, but no GaN dissociation could be detected. This broadening of the Cr/GaN interface is most likely due to two factors, the diffusion of Cr into GaN up to the solubility limit, and the roughening of the interface that occurs due to differential sputtering of the layers. For furnace anneals up to 400°C, there was no change in the Cr/GaN interface when compared to the as-deposited case. This was in contrast to the Cr/Au interface which did not noticeably broaden to levels detectable in AES depth profiles at 200°C, but at 400°C Cr diffused through the Au capping layer to form a surface oxide layer. This is similar to the case of Ni in the Ni/Au contacts. The I-V data for all these samples were similar to the as-deposited data in current magnitude. Overall, the diffusion of Cr to the Au/ambient surface did not result in better contact properties, presumably due to the lack of continued reaction at the Cr/GaN interface at the temperatures studied.

While the Cr/Au contact results were rectifying for anneal temperatures of 400°C or less, a 900°C, 15 second RTA resulted in ohmic contacts (Figure 5.21). The specific contact resistance reported above was calculated from the current (11.4 mA) at 5V and using Ohm's law, with the resistance being multiplied by the area of the dot contacts ($1.96 \times 10^{-3} \text{ cm}^2$) to give $\rho_c = 4.3 \times 10^{-1} \text{ } \Omega \text{cm}^2$. In this procedure,

the bulk resistance of the GaN is assumed to be zero. Since ρ_{GaN} is finite, the actual specific contact resistance is lower than the value reported above. In any case, $\rho_c < 10^{-4}$ is desired for practical devices.

For the RTA sample, an AES depth profile (Figure 5.25) showed widespread diffusion of Cr throughout the entire structure along with GaN dissociation. The varying layer thickness across the contact evident in the XTEM micrograph (Figure 5.29) is due to the intermixing of Au and Cr which is also shown in the depth profile. As opposed to the as-deposited sample, ion milling did not effect the thickness of the metal layers as shown by the remaining glue at the metal surface. In this contact scheme, much like the Ni/Au scheme, dissociation of GaN took place with Ga diffusion through the contact layers. The Ga diffused to the surface in some regions as evidenced by EDS data, and Ga also segregated into the Au region of the contact as was seen in the AES depth profile.

For the RTA sample, both a AES depth profile (Figure 5.25) and a XTEM micrograph (Figure 5.29) coupled with EDS data (Figure 5.32) indicated Ga levels at the surface of the contact without comparable levels of N, which is consistent with GaN dissociation. There was however, one discrepancy between the two sets of data. While the XTEM and EDS showed a strong Ga signal at the surface with no evidence of Ga throughout the contact layer, the AES data indicated a

chromium oxide with only a slight Ga signal at the surface, and a large accumulation of Ga in the original Au region of the contact. This variation can be explained in terms of spot size and sampling area of the two techniques. In the EDS, the spot size was $\sim 500\text{\AA}$ which allowed for the effects of surface roughness to be negligible for this measurement. On the other hand, the spot size for the AES was $\sim 1\mu\text{m}$. Over this large an area, the surface roughness evident from Figure 5.29 leads to data collection from different depths relative to the original surface and the formation of profiling artifacts which complicate data analysis.

To understand the mechanism responsible for the increased conduction, it is important to first look at the properties of Cr in GaAs and relate them to Cr in GaN. In GaAs, chromium is a very deep acceptor ($E_v + 0.79\text{ eV}$) that is generally used to make semi-insulating GaAs [Mil73] by substituting on the Ga site in the lattice [Bro78 and Eu80]. Yu et al. determined that diffusion of Cr atoms in GaAs results from a substitutional Cr hopping into an interstitial site, rapid migration of the interstitial atom, and a subsequent return to a vacant Ga site [Yu91], thus the Ga vacancy concentration and vacancy generation rates are key factors in this substitutional-interstitial conversion process [Dea86]. Based on these data from GaAs, it is proposed that the 900°C , 15 second RTA caused diffusion of Cr into GaN. Since Cr acts as an acceptor when substituted

on the Ga sublattice in GaAs, it is reasonable to believe it would behave similarly in the III-V material GaN. This is consistent with the fact that Cr diffused into the GaN at 400°C which led to lower breakdown voltages (~1V) than predicted from the Schottky model (2.2-3.0 V). At 900°C, GaN dissociation occurred with out-diffusion of Ga resulting in a Ga vacancy flux which when combined with interstitial Cr diffusion, could create substitutional Cr deep acceptors over the depletion depth and increase the near-surface hopping conduction. Contrary to the GaAs/Ni/Ge/Au system [KimT90], there was no evidence of solid phase regrowth of the GaN at the contact interface in any of the XTEM micrographs. Thus the increased doping levels are attributed to Cr interstitial in-diffusion as opposed to solid phase regrowth with interstitial transport enabling this mechanism.

In these contacts, it has been proposed that substitutional acceptor Cr impurities in the GaN are contributing to the conductivity by increasing the carrier concentration in this region. Presumably, the Cr impurity level in GaN will be quite deep and thus the problem arises as to how the Cr acceptors will participate in conduction since at room or device operation temperature there will not be enough thermal energy to excite a large percentage of carriers between the Cr acceptor level and the valence band. The method of conduction proposed for this situation in

hopping conduction between Cr acceptor levels without excitation into the valence band.

For hopping conduction to occur, there is an activation energy, usually smaller than the band to band activation energy, that must be overcome. This energy arises due to the dispersion of impurity levels. By increasing the impurity concentration, this activation energy can be decreased until eventually it vanishes which corresponds to the transition between activated and metallic conduction. The concentrations that were dealt with in this study were far below this level. The physical reason for the exponential dependence of carrier hopping results from the probability of a jump between two impurities being determined by the wave function overlap. The wave function overlap integrals drop exponentially with increasing distance between impurities. As the concentration decreases, the mean inter-impurity separation increases, with the jump probability and hence the electrical conductivity decreasing exponentially [Shk84]. Hopping conductivity has been shown in a variety of wide band gap semiconductors including ZnSe [Mark95] and GaAs [Loo90].

Another potential explanation, which will be shown to be inaccurate, for the observed increase in conduction in the contacts following the 900°C heat treatment was that elevated temperature caused the formation of N vacancies in the GaN which led to a type shifting from p- to n-GaN. If

this were true, a low resistance contact to n-GaN was formed as opposed to the desired contact to p-GaN. A recent report has shown that through the use of an AlN capping layer, ohmic behavior was reduced in n-GaN as opposed to an uncapped sample upon heating to 1100°C. This was attributed to the formation of N vacancies in the uncapped sample which increased the near-surface donor concentration [Zol96b].

To determine the effect of heat treatment on the doping character of the GaN, photoluminescence (PL) and Hall effect measurements were performed on a sample as-grown, and following a 900°C, 15 second RTA in flowing N₂. The PL spectra from 350-650 nm (3.54-1.90 eV) for these samples can be seen in Figure 5.38. In this figure, the peak of the strongest transition is at 2.83 eV (438 nm) for the as-grown sample and 2.93 eV (423 nm) for the heat treated sample. This emission is associated with a deep Mg complex which has been previously determined to have an energy of -2.87 eV (432 nm) [Myo96]. This data shows the continued presence of these Mg complexes in the material. Another important region of the spectrum is near the band gap of GaN. For this region, Figure 5.39 shows the photo emission from 355-380 nm (3.49-3.26 eV). The peak in each spectrum at 3.44 eV (360 nm) is attributed to the band edge excitation from the valence band to the conduction band, while the peak at 3.33 eV (372 nm) is attributed to an acceptor bound excitation emitted from a Mg acceptor site. More importantly, the two

curves are very similar in this low wavelength region and there is no large donor band emission in either sample that would indicate n-type conductivity in the material. The donor Si in GaN has a binding energy of ~ 30 meV which should result in a peak at ~ 363 nm; none is observed either before or after RTA.

To further demonstrate that the 900°C , 15 second RTA did not convert the surface to n-GaN, Hall data were collected from a sample as-grown and after RTA. Assuming a doped layer thickness of $1000\text{\AA}$, the calculated free carrier concentration was $2.6 \times 10^{18} \text{ cm}^{-3}$ as-grown and $4.5 \times 10^{18} \text{ cm}^{-3}$ following the heat treatment, in both cases p-type. This showed that the material did not become n-type following the heat treatment and actually had more free carriers than in the as-grown case. This can be attributed to either experimental error or some activation of Mg acceptors at this temperature, possibly by dissociating H-Mg complexes. Thus it has been shown that any conversion from p- to n-GaN would require a higher heat treatment temperature and possibly a different heat treatment environment.

Temperature Dependent I-V

Temperature dependent I-V data were used to determine the dominant transport mechanism(s) in the Ni/Au, Pd/Au and Cr/Au contacts to p-GaN. As described in Chapter 2, the tunneling parameter E_{00} can be used as a measure of the

relative importance of thermionic versus field emission transport. Since all contact metallizations were deposited on separate pieces of GaN grown on the same piece of sapphire, the theoretical value of E_{00} should be constant for each of the metallizations. From Equation 2.13, the theoretical value of E_{00} is 0.00223 eV for contacts to GaN. For ohmic contacts it is preferable that $E_{00} \ll kT$. Unfortunately, for these contacts, $E_{00} \approx kT$ for all temperatures investigated, which results in the prediction that thermionic emission should dominate conduction in each of the contact schemes. This is understandable since the hole concentration of the GaN is relatively low ($9.8 \times 10^{16} \text{ cm}^{-3}$). However, if the near-surface carrier concentration was increased due to interfacial reactions, the dominant conduction mechanisms would be expected to change.

For contacts dominated by thermionic emission of holes over the valence band offset, the saturation current is described by Equation 2.7 which can be rearranged in the following way:

$$\ln(I_0/T^2) = \ln(SA^*) + (\Delta\Phi_b - \Phi_b) / kT. \quad (5.1)$$

From this equation, plotting the temperature dependent I-V data as $\ln(I_0/T^2)$ vs $1/T$ should produce a straight line if thermionic emission was the only mechanism resulting in conduction. These data are plotted for select voltages for each of the contact schemes from 100-400K in Figure 5.40 and from 300-400K in Figure 5.41. On the other hand, if

conduction is dominated by field emission, Equation 4.1 can be used where a plot of $\ln(I)$ vs V will be linear; this is shown from 0-5 V in Figure 5.42, and from 3-5 V in Figure 5.43.

For the Ni/Au contacts Figure 5.35 showed that at a constant voltage, current increased with increasing temperature, this is consistent with thermionic emission. From Figures 5.40-5.43, the data indicates that thermionic emission is dominating conduction for low voltages and normal operating temperatures (300-400 K), whereas at reverse bias ≥ 3.0 V there is an increased field emission component.

For the Pd/Au contacts it is important to note that the sample analyzed was heat treated at 600°C, a temperature at which the GaN was not expected to dissociate. This was also not the optimum heat treatment in terms of limiting breakdown voltage. Figure 5.36 indicates thermionic emission dominates due to the very low current levels at 90 K and the tremendous increase at 390 K. From the data in Figures 5.39-5.42, it is evident that at low values of reverse bias thermionic emission is dominating the conduction. However, upon reaching a value of ≈ 3 V, field emission currents play a role in the conduction. This impact is smaller than in the Ni/Au contacts.

The Cr/Au sample was also heat treated at 600°C, a temperature at which a non-linear room temperature I-V curve

was obtained. However, this contact scheme showed that tunneling dominated more than for the other schemes. Figure 5.37 showed nearly temperature independent I-V curves over the temperature range 80-380 K, which suggests control by field emission. From Figure 5.40, the $\ln(I_0/T^2)$ vs $1/T$ plot showed slight but steady curvature at a constant temperature as the voltage was increased, and in Figure 5.42 for Cr/Au, linear $\ln(I)$ vs V was obtained for 2-5 V. It is thus believed that field emission currents play a much larger role in the Cr/Au contacts than the other contact schemes and for $V \geq 3V$, this mechanism clearly dominates transport.

Summary

Formation of electrical contacts to magnesium doped p-GaN by sputter deposition of Au and electron beam deposition of Pd/Au, Ni/Au, Ni/C/Au and Cr/Au thin film contacts was demonstrated. The best contact schemes to p-GaN took advantage of interfacial reactions between the metals and the semiconductor, in particular dissociation of GaN leading to Ga out-diffusion. Pure Au contacts showed no reaction with GaN up to 400°C and resulted only in rectifying contacts. Pd/Au contacts were rectifying under all process conditions and increased conduction was attributed to dissociation of the GaN following a 900°C 15 second RTA, with Pd or C potentially acting as an acceptor. Insertion

of a Ni interfacial layer to form a Ni/Au contact led to dissociation of the GaN at 600°C and while ohmic contacts were not obtained, the nearly-linear I-V curves were attributed to increased doping of the GaN near-surface region by interfacial carbon contamination or possibly Ni acting as an acceptor. Introduction of an intermediate C layer between Ni and Au to form a Ni/C/Au contact did not improve the contact resistance. Films of Cr/Au provided the best ohmic contacts with $\rho_c \leq 4.3 \times 10^{-1} \text{ } \Omega \text{cm}^2$ following a 900°C, 15 second rapid thermal anneal. At this temperature Cr caused the dissociation of GaN and was postulated to act as a substitutional acceptor sitting on the Ga sublattice. GaN doping was postulated to occur by an interstitialcy diffusion mechanism based on similar data for Cr in GaAs. Temperature dependent I-V measurements showed Ni/Au, Pd/Au and Cr/Au to all have components of both thermionic emission and field emission, with Cr/Au being dominated by field emission. This is consistent with the dissociation of GaN by Cr and enhanced diffusion to create increased doping in the near-surface region.

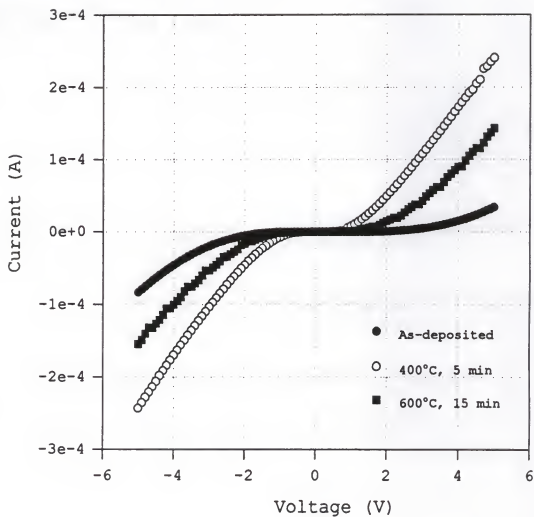


Figure 5.1. I-V curves for sputtered Au contacts to p-GaN heat treated in forming gas.

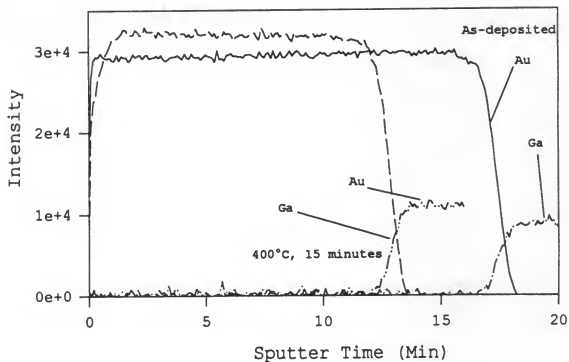


Figure 5.2. AES depth profiles for Au/p-GaN contacts as-deposited and heat treated for 15 minutes in forming gas.

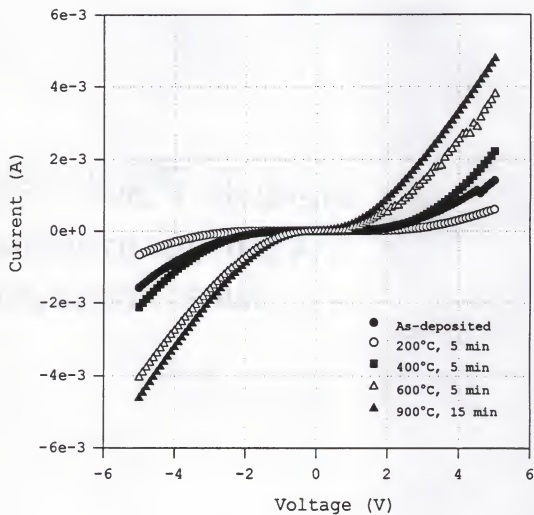


Figure 5.3. I-V data for Pd/Au on p-GaN.

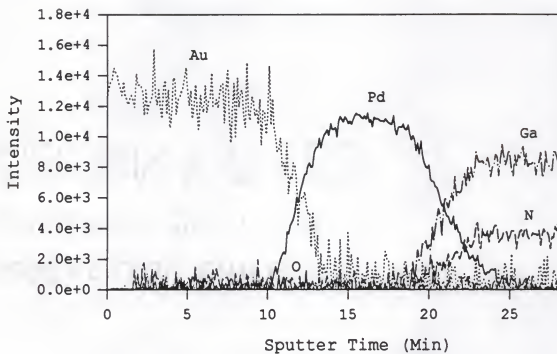


Figure 5.4. AES depth profile for Pd/Au on p-GaN, as-deposited.

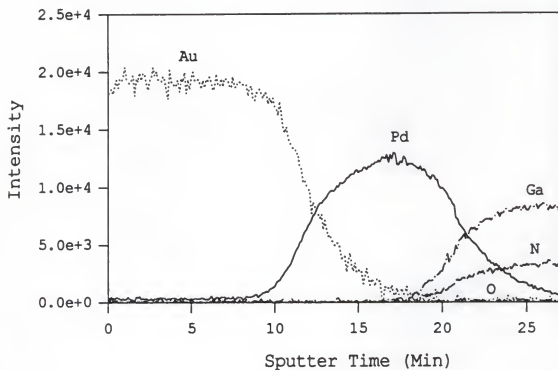


Figure 5.5. AES depth profile for Pd/Au on p-GaN, heat treated at 200°C, 5 minutes in N_2 .

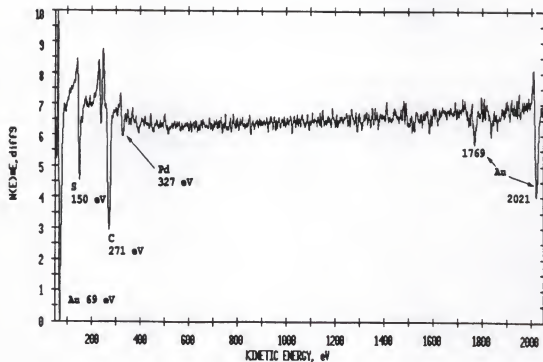


Figure 5.6. AES surface survey spectrum for Pd/Au on p-GaN heat treated at 200°C for 5 minutes, showing the Pd 327 eV peak at the surface.

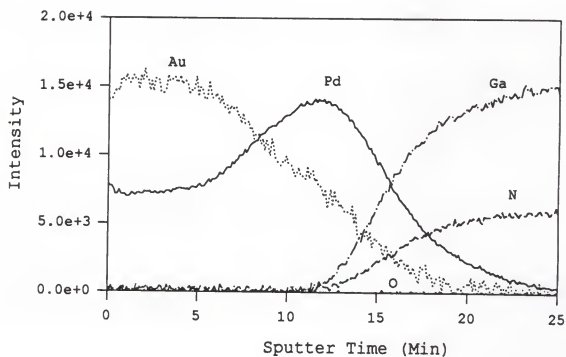


Figure 5.7. AES depth profile for Pd/Au on p-GaN, heat treated at 400°C, 5 minutes in N₂.

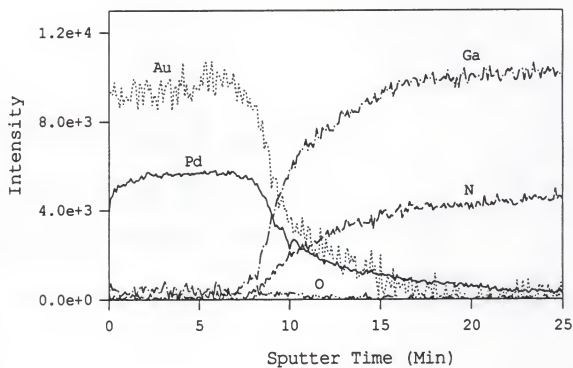


Figure 5.8. AES depth profile for Pd/Au on p-GaN, heat treated at 900°C, 15 seconds in N₂.

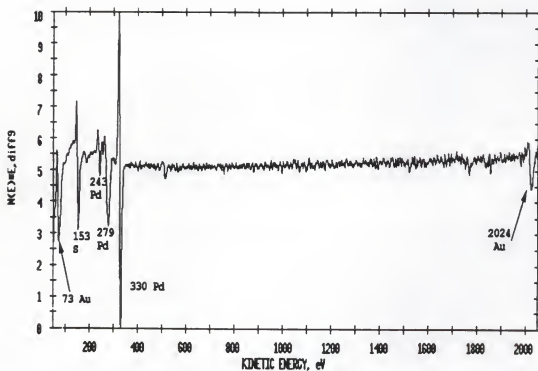


Figure 5.9. AES surface survey spectrum for Pd/Au on p-GaN, 900°C, 15 seconds in N₂, showing only Au and Pd present in this area.

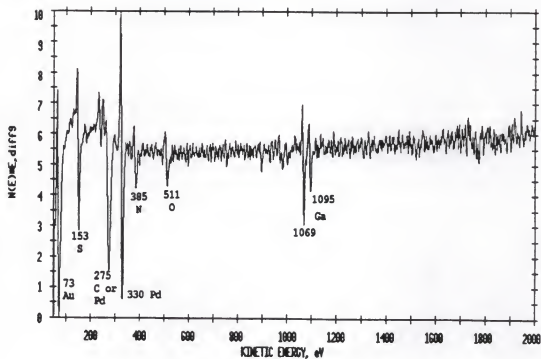


Figure 5.10. AES surface survey spectrum for Pd/Au on p-GaN, 900°C, 15 seconds in N_2 , showing Au, Pd, Ga and N present in this area.

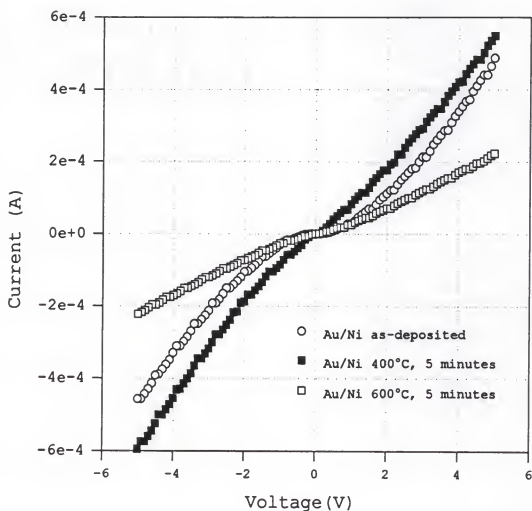


Figure 5.11. I-V curves for sputter deposited Au on electron beam evaporated Ni (2400/500Å) contacts to p-GaN, heat treated in forming gas.

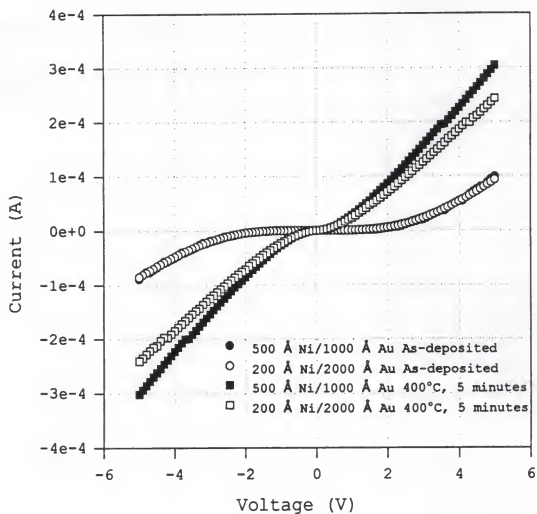


Figure 5.12. I-V curves for Ni/Au contacts to p-GaN with varying layer thicknesses.

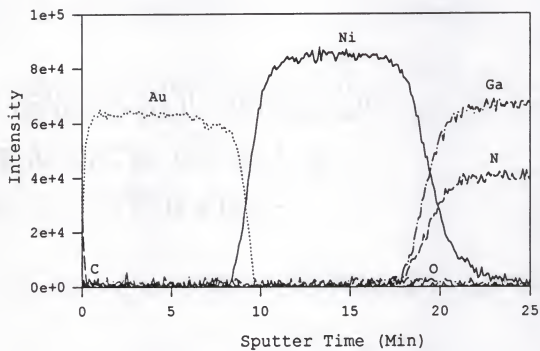


Figure 5.13. AES depth profile for Ni/Au on p-GaN, as-deposited.

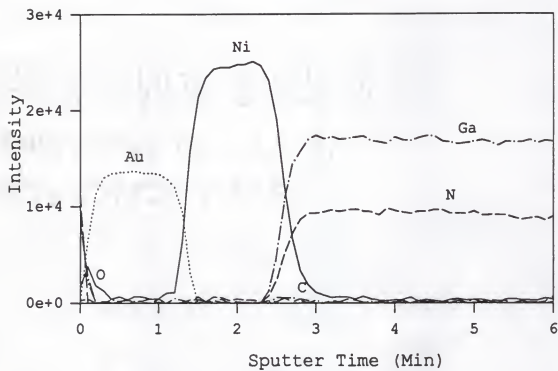


Figure 5.14. AES depth profile for Ni/Au (500/1000Å) on p-GaN, heat treated at 400°C, 5 minutes in N₂.

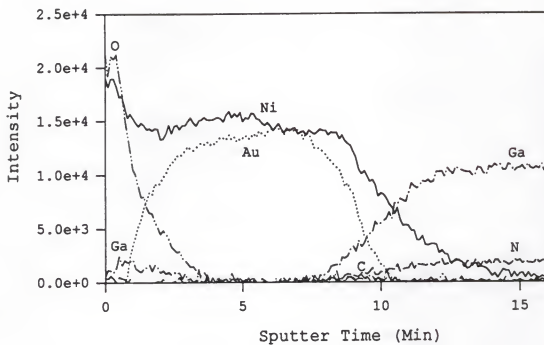


Figure 5.15. AES depth profile for Ni/Au on p-GaN, heat treated at 600°C, 30 minutes in forming gas.

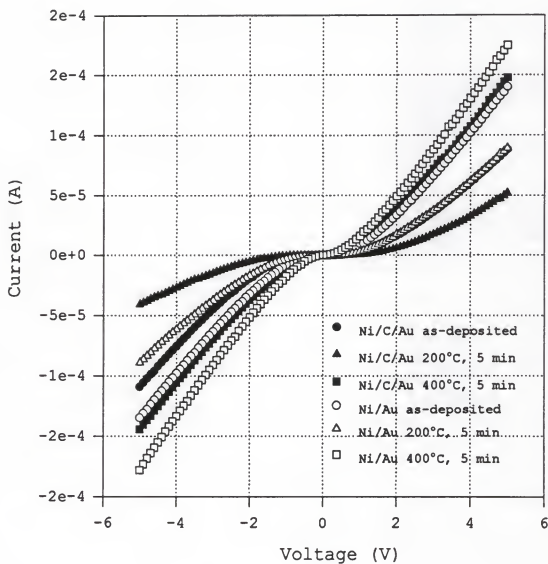


Figure 5.16. I-V curves for Ni/Au and Ni/C/Au on p-GaN.

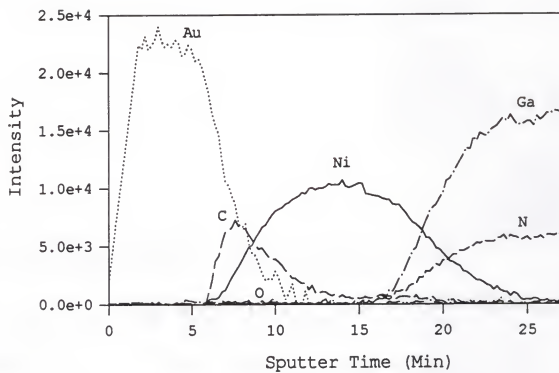


Figure 5.17. AES depth profile for Ni/C/Au on p-GaN, as-deposited.

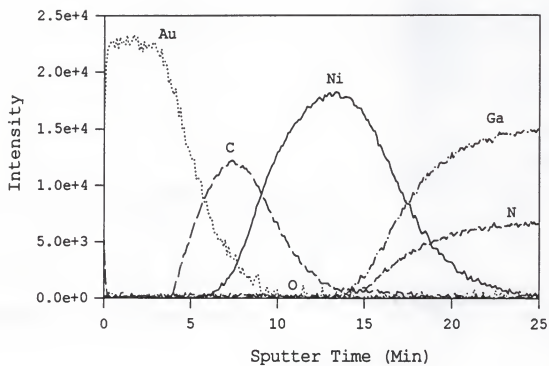


Figure 5.18. AES depth profile for Ni/C/Au on p-GaN, heat treated at 400°C for 30 minutes in forming gas.

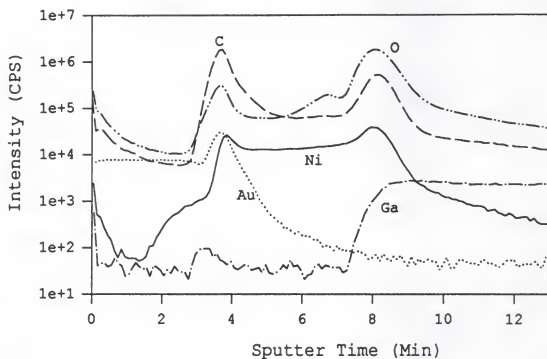


Figure 5.19. SIMS depth profile for Ni/C/Au on p-GaN, as-deposited.

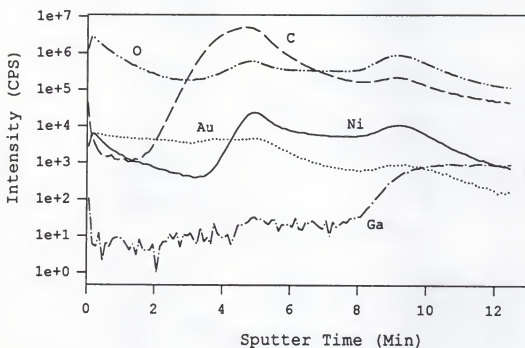


Figure 5.20. SIMS depth profile for Ni/C/Au on p-GaN, heat treated at 400°C, 30 minutes in forming gas.

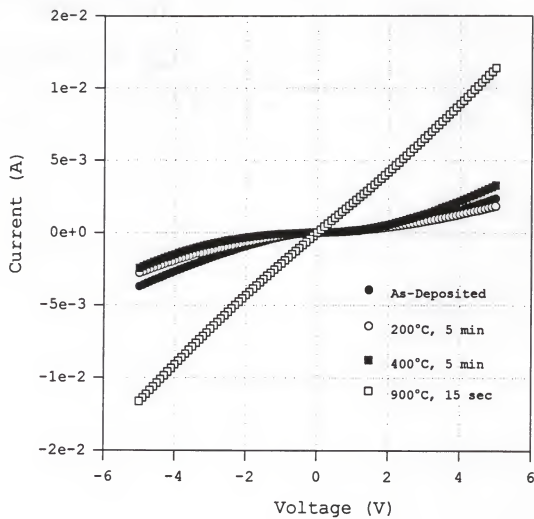


Figure 5.21. I-V data for Cr/Au on p-GaN.

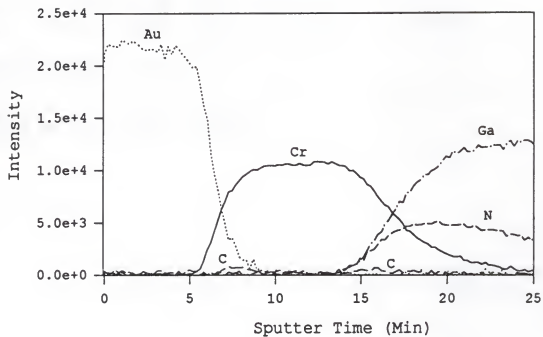


Figure 5.22. AES depth profile for Cr/Au on p-GaN, as-deposited.

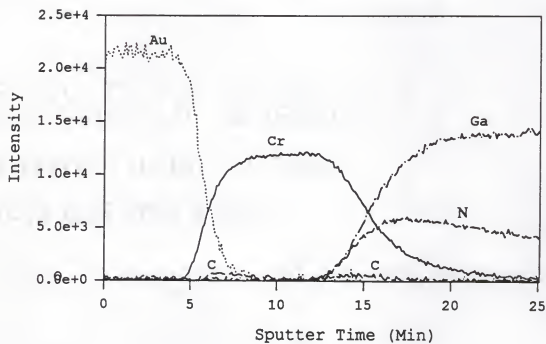


Figure 5.23. AES depth profile for Cr/Au on p-GaN, heat treated at 200°C for 5 minutes in N₂.

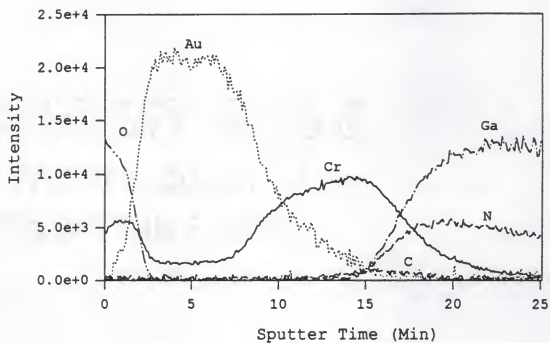


Figure 5.24. AES depth profile for Cr/Au on p-GaN, heat treated at 400°C for 5 minutes in N_2 .

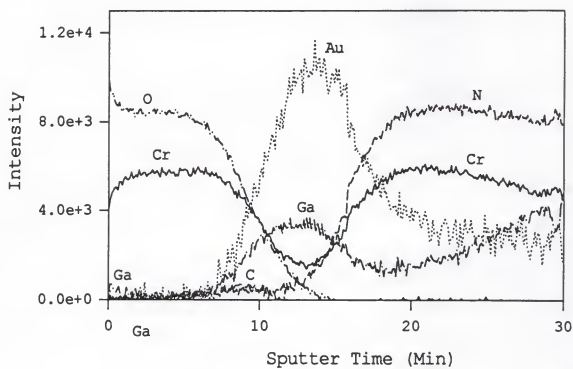


Figure 5.25. AES depth profile for Cr/Au on p-GaN, heat treated at 900°C for 15 seconds in N_2 .



Figure 5.26. Low magnification XTEM (x73K) of Cr/Au on p-GaN, as-deposited, showing planar metal layers.



Figure 5.27. SADP from an as-deposited Cr/Au contact.

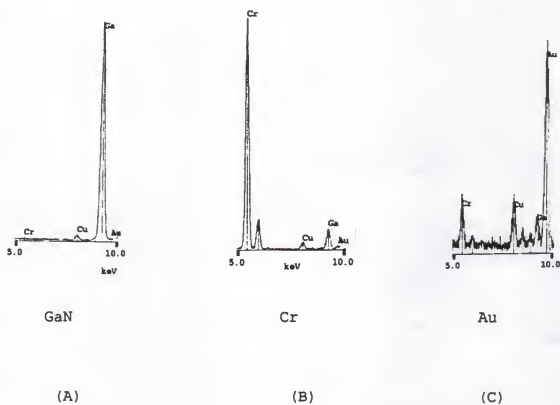


Figure 5.28. EDS data for the regions indicated from Figure 5.26.

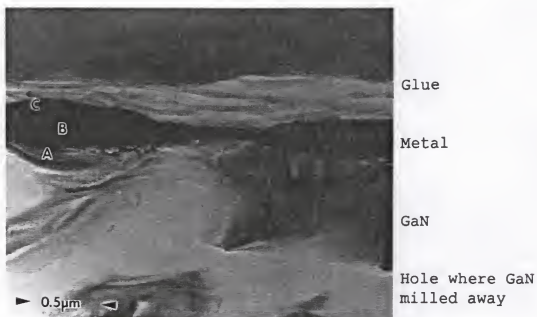


Figure 5.29. Low magnification (x20K) XTEM for Cr/Au on p-GaN heat treated at 900°C for 15 seconds in N_2 .

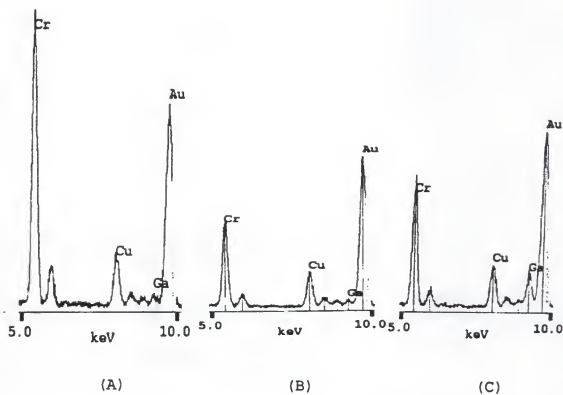


Figure 5.30. EDS data for Cr/Au on p-GaN, 900°C, 15 seconds progressing across the metal layers from the bulk to the surface.



Figure 5.31. High resolution XTEM of Cr/Au on p-GaN heat treated at 900°C for 15 seconds showing Ga surface segregation.

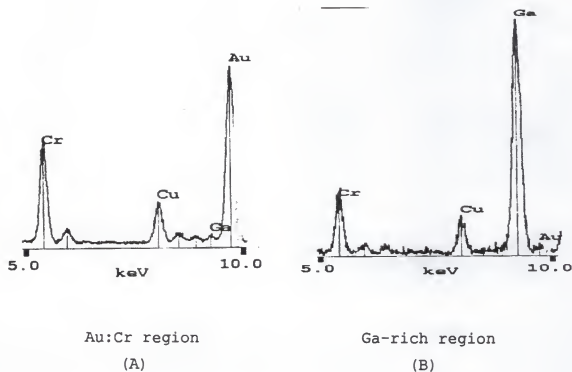


Figure 5.32. EDS data for Cr/Au on p-GaN, 900°C, 15 seconds for the micrograph in Figure 5.31.



Figure 5.33. SADP from Cr/Au on p-GaN heat treated at 900°C for 15 seconds showing Au and Cr.

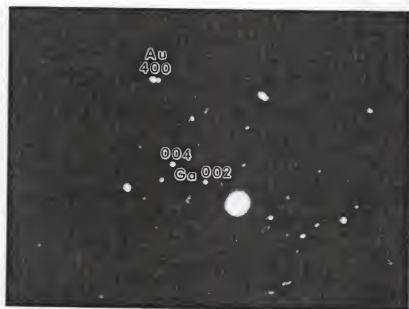


Figure 5.34 . SADP from Cr/Au on p-GaN heat treated at 900°C for 15 seconds showing Ga-rich phase.

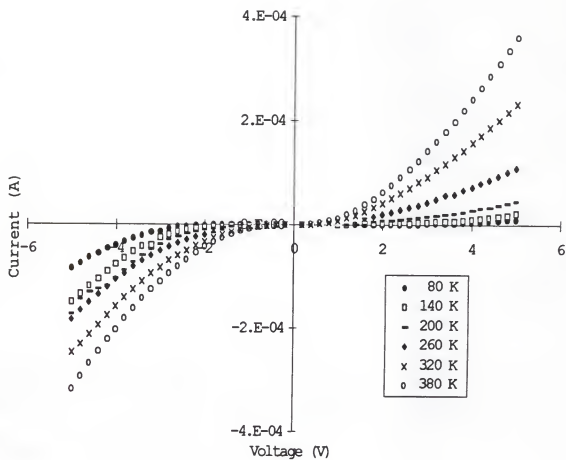


Figure 5.35. Temperature dependent I-V for Ni/Au on p-GaN, heat treated at 600°C for 5 minutes.

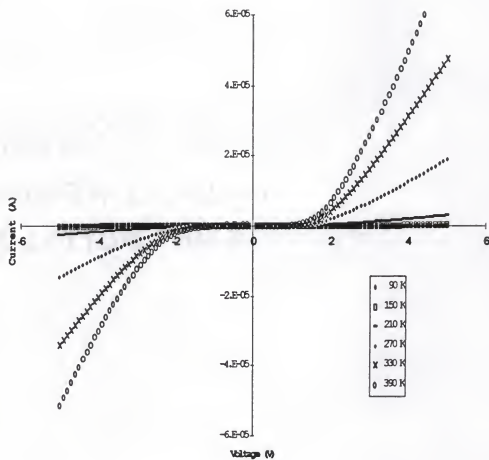


Figure 5.36. Temperature dependent I-V for Pd/Au on p-GaN, heat treated at 600°C for 5 minutes.

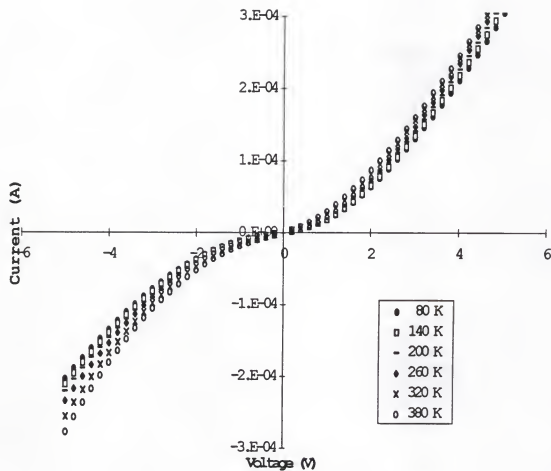


Figure 5.37. Temperature dependent I-V for Cr/Au on p-GaN, heat treated at 600°C for 5 minutes.

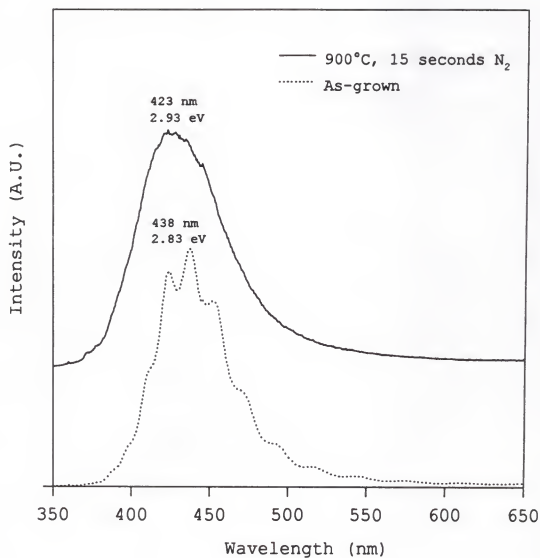


Figure 5.38. PL data for p-GaN sample as-grown and following a 900°C, 15 second heat treatment showing levels from Mg complexes.

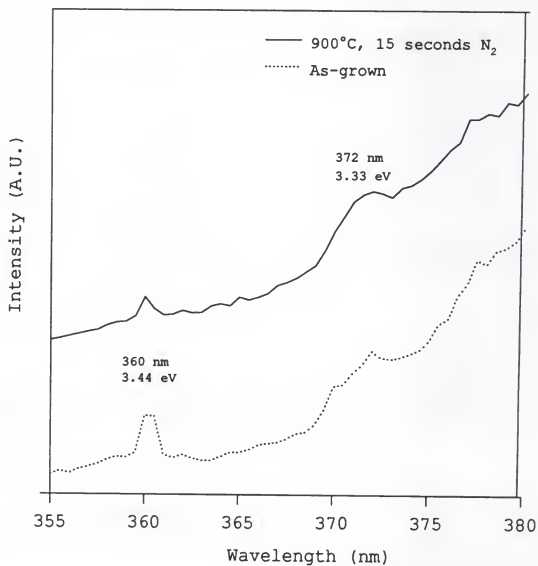


Figure 5.39. PL data for p-GaN sample as-grown and following a 900°C, 15 second heat treatment showing energy region near the bandgap.

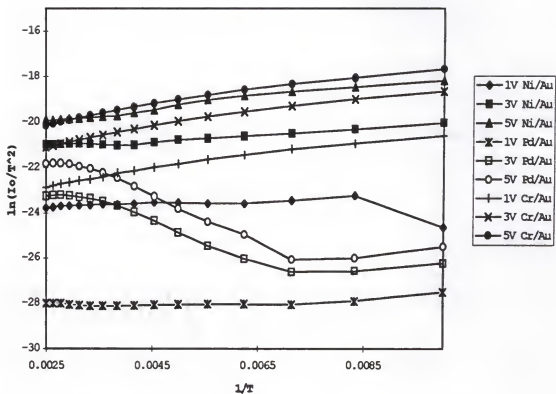


Figure 5.40. Plot of $\ln(I_o/T^2)$ vs $1/T$ from 100-400 K for contacts to p-GaN.

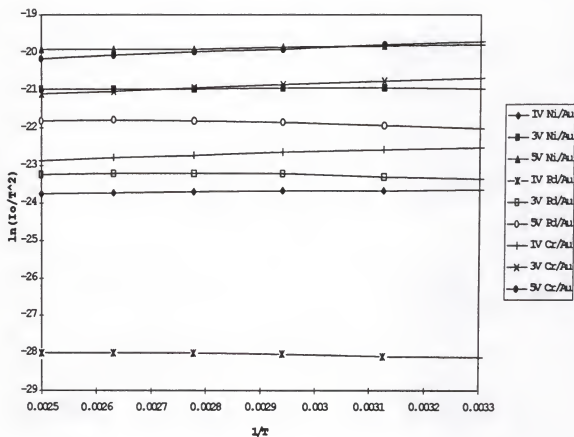


Figure 5.41. Plot of $\ln(I_o/T^2)$ vs $1/T$ from 300-400 K for contacts to p-GaN.

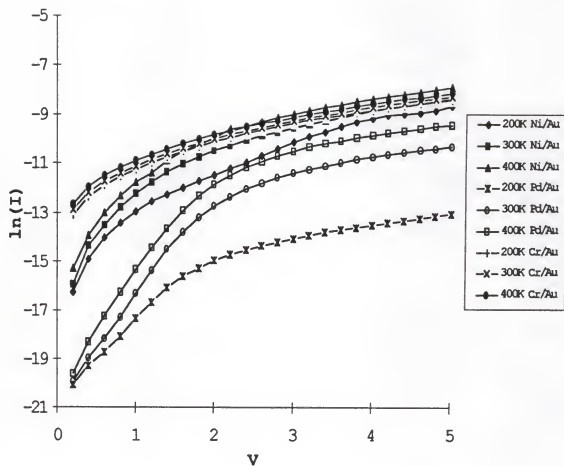


Figure 5.42. Plot of $\ln(I)$ vs V from 0-5 V for contacts to p-GaN.

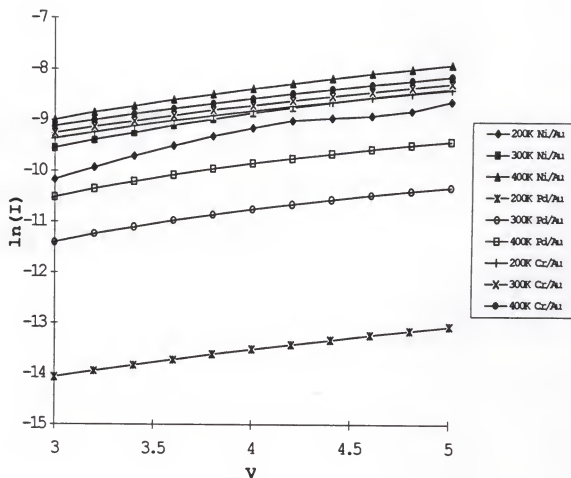


Figure 5.43. Plot of $\ln(I)$ vs V from 3-5 V for contacts to p-GaN.

CHAPTER 6 CONCLUSIONS

p-ZnTe Contacts

The formation and characterization of sputter deposited Au contacts to nitrogen doped p-ZnTe was demonstrated. Based on current-voltage data, the electrical properties of the contacts were rectifying as-deposited with a breakdown voltage of 0.5 V. These values are close to the value of 0.66 eV predicted using the Schottky model which strongly suggests the Fermi level was not pinned in ZnTe.

Upon heating at $T \geq 200^\circ\text{C}$, ohmic behavior was observed from the I-V data. Through the use of AES and SIMS depth profiles, this ohmic behavior was credited to the creation of near-surface acceptors due to doping of Au ($E_v = +272$ meV) without interfacial phase formation. This led to increased conductivity through the near surface layer, presumably by carrier hopping between deep levels in the lattice. A maximum current density of 2.3 A/cm^2 at 5 V was obtained following a 250°C , 15 minute heat treatment in forming gas. At 350°C diffusion of Au was extensive and resulted in compound formation, proposed to be AuTe_2 , which led to severe degradation of the contact properties.

Thus for Au/p-ZnTe contacts, diffusion of Au at $T \leq 250^\circ\text{C}$ formed ohmic contacts, while at 350°C , high resistivity contacts were obtained due to widespread Au diffusion and compound formation.

p-GaN Contacts

For contacts to p-GaN, the large band gap ($E_g = 3.4$ eV) and electron affinity ($\chi = 3.3\text{--}4.1$ eV) required interfacial reactions to take place for an ohmic contact to be formed. The best contact schemes to p-GaN took advantage of dissociation of the GaN to allow for increased doping of the semiconductor near-surface region. Au contacts were sputter deposited and Pd/Au, Ni/Au, Ni/C/Au and Cr/Au were deposited by electron beam evaporation onto Mg doped p-GaN.

I-V data showed rectifying contacts for all metal schemes as-deposited. Pure Au contacts showed no reaction with GaN up to 400°C and resulted in rectifying behavior. Pd/Au contacts were rectifying under all process conditions with increased conduction attributed to breakup of the interfacial oxide below 400°C and dissociation of the GaN following a 900°C , 15 second RTA heat treatment, with Pd or C potentially acting as an acceptor.

Insertion of a Ni layer to form a Ni/Au contact led to nearly linear I-V curves and dissociation of the GaN as evidenced by AES depth profiles at 600°C . The increased

conductivity was attributed to increased doping of the GaN near-surface region by interfacial carbon or Ni acting as an acceptor in the GaN lattice. Introduction of an intermediate C layer to form a Ni/C/Au contact did not decrease the contact resistance.

Films of Cr/Au provided the best ohmic contacts with $\rho_c \leq 4.3 \times 10^{-1} \Omega \text{cm}^2$ following a 900°C, 15 second RTA. At this temperature Cr caused the dissociation of GaN and was postulated to act as a substitutional acceptor sitting on the Ga sublattice. GaN doping was postulated to occur by an interstitialcy diffusion mechanism based on similar data for Cr in GaAs. This led to significant reduction of the depletion layer thickness and better carrier transport.

Temperature dependent I-V measurements showed Ni/Au, Pd/Au and Cr/Au to all have components of both thermionic and field emission, with Cr being dominated at RT by field emission. This is consistent with the dissociation of GaN by Cr and enhanced diffusion to create increased doping in the near-surface region.

CHAPTER 7 FUTURE WORK

p-ZnTe Contacts

For contacts to p-ZnTe, work must be continued to find a contact scheme that provides low resistance thermally stable contacts. Au has been shown to form ohmic contacts to p-ZnTe, but the contact resistance is too high for practical devices. Unfortunately, there will probably not be a large interest in continued work with this semiconductor due to the move within the industry away from II-VI materials and towards III-V materials.

p-GaN Contacts

The advent of blue laser diodes made from GaN requires that the study of ohmic contacts to the p-type material continue until a suitable low resistance contact is found. One possible contact scheme for these low resistance contacts will include a doping layer, such as Mg, in the contact scheme in an effort to increase the near-surface carrier concentration. If this method does not prove feasible, p-GaN contacts will most likely need to be formed

using an MBE process, similar to that used in ZnSe. It is believed that a simple metal contact scheme will not be able to provide the low resistance contacts needed for practical devices, and thus the contact scheme will have to consist of a graded region between the GaN and a semiconductor that can be very highly doped p-type, for example GaAs.

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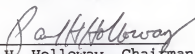
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BIOGRAPHICAL SKETCH

Jeffrey Todd Trexler was born on October 15, 1970, in Allentown, PA, and was raised in Bethlehem, PA. He graduated from Freedom High School in 1988. Upon completing high school he enrolled at Clemson University in Clemson, SC, and majored in ceramic engineering. In May of 1992, he graduated cum laude from Clemson University with a bachelor's degree. In August of 1992, Jeffrey began graduate school at the University of Florida in Gainesville, FL, majoring in materials science and engineering. Under the supervision of Dr. Paul Holloway, Jeffrey received his master's degree in materials science and engineering in May 1996 and his PhD in materials science and engineering in December 1997.

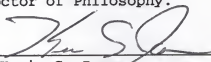
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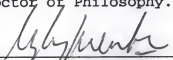
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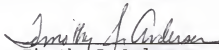
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Kevin S. Jones
Associate Professor of
Materials Science and
Engineering

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Stephen J. Pearton
Professor of Materials
Science and Engineering

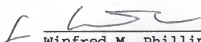
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Timothy J. Anderson
Professor of Chemical
Engineering

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1997



Winfred M. Phillips
Dean, College of
Engineering

Karen A. Holbrook
Dean, Graduate School

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